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THE

METALLURGY OF LEAD,

INCLUDING

DESILVERIZATION AND CUPELLATION.

By JOHN PERCY, M.D., F.R.S.,

LECTURER ON METALLURGY AT THE ROYAL SCHOOL OF MINES,
AND TO THE ADVANCED CLASS OF ARTILLERY OFFICERS AT THE ROYAL ARTILLERY INSTITUTION, WOOLWICH.

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TO

SIR RODERICK IMPEY MURCHISON, BART.,

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MEMBER OF THE INSTITUTE OF FRANCE,

DIRECTOR-GENERAL OF THE GEOLOGICAL SURVEY OF THE UNITED KINGDOM,

AND

DIRECTOR OF THE ROYAL SCHOOL OF MINES, ETC.,

This Volume is dedicated

WITH THE SINCERE REGARD OF

THE AUTHOR.

PREFACE.

It was intended that this volume should contain the Metallurgy of Lead, Silver, and Gold; but it has been found impossible to treat those important subjects in a sufficiently detailed and comprehensive manner in a single volume without making it so thick and heavy as to be inconvenient. It has, therefore, been decided to restrict this volume to the Metallurgy of Lead, including the processes of Desilverization and Cupellation. The Author does not regret the change in the plan of publication, because the delay in publishing the Metallurgy of Silver and Gold will, there is reason to hope, enable him to procure valuable and additional information from California and elsewhere on those subjects for the next volume, of which a considerable portion is already in print.

The Author has great pleasure in acknowledging the assistance which he has received from British Lead-Smelters, foreign Metallurgists, and others; and, so far as he is aware, he has not omitted in a single instance to record the names of individuals who have aided him in his task, except when enjoined not to do so. In this place it is proper to mention that the article on the Assay of Lead Ores has, for the most part, been prepared by Mr. Richard Smith, who is engaged as instructor in the Metallurgical Laboratory of the Royal School of Mines, and that to him, as well as his friend, Mr. H. Bauerman, the Author is much indebted for valuable assistance in passing this volume through the press.

The first two volumes of this work having been long out of print, the Author may state that he has been assiduously engaged in collecting materials for new editions of both; but so much time and labour are required in preparing such editions for the press, that he has not been able to proceed with their revision and the production of the remaining volumes as rapidly as he could have desired. New editions, however, of those volumes will appear with as little delay as possible, and, on publication, they will be found greatly altered, and, the Author ventures to hope, greatly improved.

London, August, 1870.

CONTENTS.

LEAD.

HISTORY.

PHYSICAL PROPERTIES OF LEAD.

	Page		Page
Colour	1	Specific heat	8
Lustre	1	Dilatation by heat	8
Crystalline system	1	Melting-point	8
Hardness	2	Latent heat	8
Malleability and ductility	2	Conductivity for heat and electricity	8
Specific gravity	3	Volatilization	9
Resistance to pressure	4	Other physical properties	9
Tenacity	7		

CHEMICAL PROPERTIES OF LEAD.

Atomic weight 10

LEAD AND OXYGEN.

Dioxide or Suboxide of Lead	11	Oxidizing action of Litharge on	
Protoxide of Lead	12	Sulphur	18
Heated with various metallic oxides	16	Selenium	19
Dioxide of copper	17	Tellurium	19
Protoxide of copper	17	Arsenic	19
Oxide of zinc	17	Antimony	19
Iron-scales	17	Tin	20
Sesquioxide of iron	17	Bismuth	20
Protoxide of manganese	17	Copper	21
Stannic acid	17	Zinc	21
Titanic acid	18	Iron	21
Oxide of antimony	18	Hydrated Protoxide of Lead	22
Antimonious acid	18	Sesquioxide of Lead	23
Arsenious acid	18	Red-Lead	24
Arsenic acid	18	Peroxide of Lead	24

LEAD AND SILICON.

Silicates of Protoxide of Lead	27	Heated with sesquioxide of iron and charcoal	34
Heated with sulphur	30	Silicates of protoxide of lead and potash	35
Heated with protosulphide of iron	31	Do. and soda	36
Heated with wood charcoal	31	Do. and baryta	36
Heated with carbonate of soda and charcoal, and with carbonate of lime and charcoal	33	Do. and lime	36
Heated with iron	33	Do., lime, and alumina	36

LEAD AND SULPHUR.

	Page
Sulphide of Lead	37
Heated with other metallic sulphides	38
Supposed Subsulphides of Lead	39
Sulphate of Protoxide of Lead	40
Action of hyposulphite of soda on sulphate of lead	42
Sulphate of lead heated with fixed alkaline carbonates, or with lime	42
Heated with silica and certain silicates	42
Heated with borax	43
Heated with protoxide of lead	43
Heated with chloride of lead	43
Heated with alkaline and earthy sulphates	43
Heated with chloride of sodium or potassium	43
Heated with fluoride of calcium	44
Heated with fluoride of calcium and lime	44
Heated with carbonate of lime, fluoride of calcium, and carbon	44
Heated with sulphate of baryta, sulphate of lime, and fluoride of calcium	44
Heated with lead	45
Heated with cyanide of potassium	45
Heated with iron	45
Special Reactions connected with Sulphide of Lead	45
Sulphide of lead heated with protoxide of lead	45
Heated with sulphate of lead	46
Heated with access of air	46
Heated with access of air in admixture with other sulphides	47
Heated with silicate of lead	48
Heated in the vapour of water	49
Sulphate of lead heated with carbon	51
Heated in hydrogen	52
Heated in carbonic oxide	52
Sulphide of lead heated in hydrogen	52
Heated in carbonic oxide	52
Heated with carbonate of soda or potash, or with caustic soda, or potash	53
Heated with the fixed alkalies or their carbonates and nitre, and alone with nitre or certain other oxidizing substances	53
Heated with the fixed alkalies or their carbonates and carbon	54
Heated with lime and with lime and carbon	55
Heated with baryta and with baryta and carbon	55
Heated with sesquioxide of iron	56
Heated with iron	56
Heated with oxide of iron and carbon	58
Heated with tribasic silicate of protoxide of iron	58
Heated with tin	59
Heated with copper	60
Heated with zinc	61
Heated with antimony	62
Sulphide of antimony heated with lead	62
Sulphide of arsenic heated with lead	63
Sulphide of lead heated with cyanide of potassium	63
Heated with ferrocyanide of potassium	63
Mixed with chloride of sodium and roasted with access of air	65
Heated with chloride of ammonium	66

LEAD AND CARBON.

	Page
Carbide of Lead	67
Carbonates of Protoxide of Lead	67
White-lead, cerusse, flake-white	68
Neutral carbonate of protoxide of lead	70

LEAD AND ARSENIC.

	Page
Arsenide of Lead	71
Quantity of arsenic in shot	72
Arsenites of Protoxide of Lead	73
Arseniates of Protoxide of Lead	73
Do., combined with Chloride of Lead	74

LEAD AND PHOSPHORUS.

	Page
Phosphide of Lead	74
Phosphates of Protoxide of Lead	75
Do., combined with Chloride of Lead	77

LEAD AND CHLORINE.

Page
Chloride of Lead 77
Oxychlorides of Lead 79
Manufacture of Oxychloride of Lead 81
Chlorocarbonate of Lead 84

LEAD AND NITROGEN.

Nitride of Lead 85
Nitrates of Lead 85
Neutral or mononitrate 85
Basic nitrates of protoxide of lead ... 85
Hyponitrates and nitrites of protoxide of lead 85

LEAD AND ANTIMONY.

Antimoniate of Protoxide of Lead 86

ALLOYS OF LEAD.

Lead and Potassium 88
Lead and Sodium 90
Lead and Copper 91
Lead and Manganese 93

ORES OF LEAD.

Sulphide of lead 94
Zinckenite 98
Plagionite 98
Jamesonite 98
Boulangerite 98
Geocronite 98
Kilbrickenite 98
Bournonite 98
Sulphate of lead 98
Carbonate of lead 99
Phosphate of lead 99
Arseniate of lead 100
Selenide of lead, chlorides and oxychlorides of lead, lanarkite or sulphato-carbonate of lead, and vanadinite 100
British Lead Ores 100
Proportion of Silver in British Lead Ores 102

ASSAY OF LEAD ORES.

Sampling 103
Furnace and Implements 104
Furnace, crucibles, &c. 104
Stirrer 106
Ingot-moulds 106
Hammer, forceps, and brush 106
Balance and weights 106
Fluxes and Reducing Agents 106
Carbonate of soda 106
Borax 106
Fluor-spar 106
Cream of tartar or bitartrate of potash 106
Iron 106
Assay of Galena in Iron Crucibles with addition of Fluxes 106
Assay of Galena in Iron Dishes ... 108
Assay of Lead Ores in Iron Crucibles without Fluxes 110
Assay of Lead Ores in Earthen Crucibles, with addition of Iron 110
Assay of Carbonate and Phosphate of Lead 112
Influence of non-metalliferous matters upon the yield of Lead by the method of Assay with Fluxes in the Iron Crucible 113
Carbonate of lime 113
Silica 114
Sulphate of baryta 116
Influence of Metals upon the method of Assay with Fluxes in the Iron Crucible 117
Silver 117
Gold 117
Copper 117
Zinc 118
Antimony 119
Arsenic 119
Iron 119
Wet Assay of Lead Ores 120

EXTRACTION OF SILVER FROM LEAD.

PATTINSON'S PROCESS.

	Page
History of Mr. Pattinson's invention	121
Description of the apparatus	124
Mode of conducting Pattinson's process	128
Modifications in the mode of conducting Pattinson's process	134
OBSERVATIONS ON PATTINSON'S PROCESS	136
Effect of foreign metals upon Pattinson's process	138
Proportion of skimmings and loss of lead	138
Time and labour required in Pattinson's process	139
Cost of Pattinson's process	139
Wrought-iron Pattinson-pots	139
APPLICATION OF MACHINERY TO PATTINSON'S PROCESS	140
ELIMINATION OF CERTAIN METALS FROM LEAD BY CRYSTALLIZATION	144
Copper	144
Nickel	144
Antimony, tin, arsenic	146
CONCENTRATION OF COPPER IN PATTINSON'S PROCESS	146
Do., WHETHER INFLUENCED BY THE PRESENCE OF SMALL QUANTITIES OF SULPHIDE OF LEAD AND ANTIMONY	147
EXPERIMENT ON THE EFFECT OF THE ADDITION OF A SMALL QUANTITY OF ANTIMONY UPON PATTINSON'S PROCESS	147
EXPERIMENT ON THE EFFECT OF THE ADDITION OF A SMALL QUANTITY OF TIN UPON PATTINSON'S PROCESS	148

PARKES' PROCESS.

Description of the apparatus	149
Description of the process	150
Cost of the process	153
Karsten's experiments on Parkes' process	153
Dezincification of lead by chloride of lead	160
Do. by other chlorides	161
Treatment of argentiferous zinc	163
Produce and cost of desilverization by zinc at Clausthal	165
Dezincification of desilverized lead by superheated steam	167
Later trials of Parkes' process in Prussia	171

DECOPPERIZATION OF LEAD BY ZINC.

Mode of conducting the operation 175

REFINING OR CUPELLATION.

ENGLISH CUPELLATION	178
Description of the furnace and test	178
Mode of conducting the process	183
GERMAN CUPELLATION (ABTREIBEN)	185
GERMAN CUPELLATION AT FREIBERG	186
Description of the furnace	186
Preparation of the working bottom	188
Mode of conducting the process	192
Abzug	198
Abstrich	199
Litharge	201
Elimination of antimony, copper, and iron during the process	202
Hearth-bottom	203
OBSERVATIONS ON THE PROCESS	203
ON THE PROPORTION OF SILVER CARRIED OFF BY THE LITHARGE DURING THE PROCESS	203
GERMAN CUPELLATION WITH COAL AS FUEL	204
Results of Cupellation at Friedrichshütte	208

REFINING OF "BLICKSILBER."

REFINING IN AN OPEN TEST WITH BLAST	209
Indian method	211
REFINING IN A TEST WITH BLAST UNDER A MUFFLE	212

LEAD-SMELTING.

Page
HISTORICAL NOTICES ON LEAD-SMELTING IN GREAT BRITAIN 213

INTRODUCTORY OBSERVATIONS ON LEAD-SMELTING.

Ores of lead 218
Presence of silver in the ores of lead 219
CLASSIFICATION OF SMELTING PROCESSES 219
DESULPHURIZATION OF GALENA ... 219
DEOXIDATION OF OXIDIZED ORES OF LEAD 220

AIR-REDUCTION PROCESS.

REVERBERATORY FURNACES 222
Flintshire furnace 222
Spanish furnace 222
Flowing-furnace 222
Bleiberg furnace 222
BLAST-FURNACES 222
Ore-hearth 222

SMELTING IN THE FLINTSHIRE FURNACE.

Description of the furnace 222
LEAD-SMELTING IN THE FLINTSHIRE FURNACE AT BAGILLT, NEAR HOLYWELL, FLINTSHIRE 229
Description of the process 229
ANOTHER DESCRIPTION OF LEAD-SMELTING IN THE FLINTSHIRE FURNACE 231
DESCRIPTION BY THE AUTHOR OF LEAD-SMELTING IN THE FLINTSHIRE FURNACE NEAR HOLYWELL, FLINTSHIRE 232
ANALYTICAL DATA CONCERNING LEAD-SMELTING IN THE FLINTSHIRE FURNACE 234
CONCLUSIONS FROM THE PRECEDING ANALYTICAL DATA 235
ADDITIONAL ANALYTICAL DATA CONCERNING LEAD-SMELTING IN THE FLINTSHIRE FURNACE 239
LEAD-SMELTING IN THE FLINTSHIRE FURNACE AT ALPORT, DERBYSHIRE 240
DO. IN OTHER LOCALITIES 242
Tarnowitz, Upper Silesia 242
Clausthal, Upper Harz 244
Adra, South of Spain 244
BRITTANY FURNACE 244
The "procédé breton" 244
BELGIAN FLINTSHIRE FURNACE, with two fire-places 245

SMELTING IN THE SPANISH REVERBERATORY FURNACE.

Furnace and mode of working 246
Boliche with brushwood as fuel 252
Boliche with coal as fuel 252
English furnace with coal as fuel ... 252

LEAD-SMELTING IN THE FLOWING-FURNACE.

BY THE CORNISH PROCESS 257
Calciner 257
Flowing or melting-furnace 258
Ore 259
Calcination 259
Flowing or melting 260

LEAD-SMELTING AT BLEIBERG.

Description of the furnace 262
Modification of the furnace 263
Mode of conducting the process 264
Results of smelting 266
Observations 267
Lead-assaying at Bleiberg 270

LEAD-SMELTING IN PERU.

Description of the furnace 271
Unsuccessful attempts at lead-smelting at great elevations 274

SMELTING IN THE ORE-HEARTH.

Page

Description of the ore-hearth 279
Mode of conducting the process of smelting 281
Composition of the slag 282
Results obtained from one week's smelting 283
Comparative results from smelting in the reverberatory furnace and in the ore-hearth 284
VARIATIONS IN THE CONSTRUCTION AND DIMENSIONS OF THE ORE-HEARTH 285
TREATMENT OF HEARTH-ENDS 289
AMERICAN ORE-HEARTH 289
Description of the hearth 290
Mode of conducting the process ... 291
Results of smelting in the American ore-hearth at Bleiberg in Carinthia 292
Do. at Przibram in Bohemia 293

LEAD-SMELTING IN INDIA IN SMALL BLAST-FURNACES 293

ROASTING AND DEOXIDIZING PROCESS.

LEAD-SMELTING AT SALA IN SWEDEN.

Description of the ores 296
RÅSMÄLTNING (*Raw-smelting*) 298
FÖRBLYNINGS- or so called BLYSMÄLTNING (*Lead-smelting*) 299
Products of the lead-smelting process 301
Werkbly (work-lead) 301
Skärsten (regulus) 301
Slagg (slag) 301
Wändrostning (calcination) 301
Drifning af Werkblyet (cupelling the work-lead) 301
Finering (refining) 302
Friskning af glete (reduction of the litharge) 302

LEAD-SMELTING AT FREIBERG.

Mode of occurrence and nature of the ores at Freiberg 304
The precious quartz group 304
The pyritic lead group 304
The precious lead group 304
The barytic lead group 305
Classification of ores 305
Mixture of ores 305
OPERATIONS IN THE FREIBERG PROCESS 306
Smelting certain ores in blast-furnaces 306
Smelting in blast-furnaces the regulus produced 306
Smelting slags, containing lead, in conjunction with certain ores in reverberatory furnaces 306
ORE-ROASTING OR CALCINING 307
Composition of roasted ore 308
SMELTING IN THE BLAST-FURNACE ... 309
Description of the blast-furnace ... 309
Process of smelting 309
Duration of the smelting 311
Products 312
Blast-furnace lead 312
Blast-furnace regulus 312
Speise 313
Slags 313
Other kinds of blast-furnace now in use at Freiberg, 1868 314
Stolberg furnace 314
Seven-twyer furnace 315
Lead-smelting in a seven-twyer blast-furnace in the Harz 316
SMELTING OF REGULUS 316
First smelting 316
Second smelting 317
Slags from regulus-smelting 318
SMELTING OF LEAD-SLAGS 319
Roasting 319
Description of the reverberatory smelting-furnace 319
Process of smelting 320
Regulus from slag- and ore-smelting in the reverberatory furnace 323
Slags from ditto 324
Experiments with a view to volatilize the zinc in ditto 325
ACCESSORY PRODUCTS 325
CONCLUSIONS FROM THE ANALYTICAL DATA RELATING TO THE FREIBERG PROCESS 327

Page

YIELDS AND LOSS 330
SMELTING COSTS 332
Ore-smelting in the blast-furnace 332
Slag- and ore-smelting in the reverberatory furnace 332
Smelting in the reverberatory furnace of slags from regulus-smelting 332
Regulus-smelting 333
TREATMENT OF COPPER-REGULUS..... 333
Treatment of enriched regulus in the manufacture of blue-vitriol 335
Solution 335
Crystallization 336
Economical results 337
Observations 337
PRODUCE OF THE FREIBERG MINES IN 1867 337

LEAD-SMELTING AT PONTGIBAUD.

Production of lead in France 338
Description of the ore 339
Roasting and agglomerating furnace 340
Method of proceeding 340
Blast-furnace 342
Method of proceeding 343
Regulus 343
Slags 344
Smelting costs 345
CONCLUSIONS FROM THE ANALYTICAL DATA 345

LEAD-SMELTING AT VIALAS.

Description of the process 346

LEAD-SMELTING AT LA PISE.

Description of the furnace 347

SMELTING OF THE LEAD ORES OF COMMERN.

Description of the ore, and system of dressing 351

LEAD-SMELTING AT MECHERNICH, RHENISH PRUSSIA.

Calcining and melting 353
Reduction in blast-furnaces 353
Desilverization of the lead 354

LEAD-SMELTING AT THE MÜHLENGASSE WORKS 354

LEAD-SMELTING AT MÜNSTERBUSCH, NEAR STOLBERG 355

LEAD-SMELTING AT EMS IN NASSAU 356

LEAD-SMELTING AT BURGFEY 357

IRON-REDUCTION PROCESS.

LEAD-SMELTING AT TARNOWITZ 357

Description of the low furnace 360
Method of proceeding 360
Observations 367

LEAD-SMELTING IN THE UPPER HARZ..... 368

SCHLIEG-SMELTING 370
Products of smelting 372
SMELTING OF REGULUS 379
Roasting 379
Composition of roasted regulus ... 380
Smelting of roasted lead-regulus... 382

Page
Lead from regulus-smelting 383
Regulus from lead-regulus smelting 383
Slags from lead-regulus smelting ... 383
Lead-smelting by the Iron-reduction Process in Japan 384

LEAD-SMELTING WITH BASIC SILICATE OF PROTOXIDE OF IRON.

Description of the Rachette furnace 385
Schlieg-smelting with Lime in the Rachette Furnace 392
Particulars of yield 396

LEAD-SMELTING AT PRZIBRAM, BOHEMIA.

Composition of the ores 399
Furnace 400
Spence's Process for the Treatment of Galena and Blende in intimate mixture 405
Analytical Data concerning Lead-smelting at Przibram 405
Roasted lead ores 406
Lead-regulus 406
Slag from ordinary lead-smelting at Przibram 407
On the retention of the regulus in the slag 410

SMELTING OF OXIDIZED ORES AND PRODUCTS.

Common or North of England Slag-Hearth 411
Description of the slag-hearth..... 412
Small Slag-hearths in Spain 417
The Spanish Slag-hearth 418
Description of the slag-hearth at Alport 419
Characters and composition of the slag from the Spanish slag-hearth 420
Carthagena Furnaces 421
Description of the furnace 422
Smelting-charge 423
Mode of conducting the process ... 424
Smelting costs 427
Remarks on the Carthagena furnace 427
Cost of reduction of grey-slags in the Carthagena furnace 429
Smelting of Lead Ore in which the Lead exists as Sulphate 430
Nature of the ore 430
Process of smelting 430
Theory of the process 431
Experiments on the reduction of Artificial Sulphate of Lead on the large scale in furnaces 431
Smelting of Lead Ores containing the Lead as Carbonate or Carbonate and Phosphate 433
Wet Process for extracting Lead from Carbonated Ores 434

CONDENSATION OF LEAD-FUME.

Bishop Watson's essay 434
Condensation and collection of lead-fume 436
Long Horizontal Flues..... 438
Condensing Arrangement at the Alport Lead Smelting Works, Derbyshire 438
Stagg's Condenser 441
Condensing Arrangement at Wensleydale, Yorkshire 442
Do. at the Wanlock Head Smelting Works, Dumfriesshire..... 444
Fallize's Scheme of Condensing Lead-fume..... 444
Condensing Arrangement at the Eggleston Mill, near Alston, Cumberland 447
Observations on the Condensation of Lead-smoke by a British Smelter 448
Characters and Composition of Lead-fume 451
Particular variety of fume from the blast-furnaces at Pontgibaud 454
On the presence of gold as well as silver in lead-fume 455
Remarks..... 455
Quantity of fume obtained in smelting lead ores, and in certain other metallurgical processes connected with lead 456
Treatment of lead-fume 458

SOFTENING OF HARD LEAD.

	Page
Softening of Hard Lead by Atmospheric Oxidation	459
Softening-furnace with cast-iron bottom	459
Mode of charging	461
Time required for softening	461
Poling of softened lead before pattinsonizing it	461
History of the process of softening by atmospheric oxidation	462
Softening of Hard Lead by Special Agents of Oxidation	464
Treatment of Dross obtained in Softening	466
Liquation of Hard Lead	467
Liquation and poling at the Silver Works at Schemnitz	469

REDUCTION OF LITHARGE.

	Page
Reduction in the reverberatory furnace	470
Do. in the Bleiberg furnace	473
Do. in the blast-furnace	476
Do. in the German cupellation-furnace	479
Chinese Method of Reducing Litharge	479

REMARKS ON THE VARIETY OF LEAD-SMELTING PROCESSES, AND THE INFLUENCE OF DIFFERENT FOREIGN MATTERS IN THE ORE.

	Page
Case for illustration	480
Iron-pyrites	482
Copper-pyrites	483
Sulphide of zinc	484
Sulphide of antimony	485
Arsenic	486
Sulphide of silver	486
Silica	487
Carbonate of lime	487
Dolomite	488
Carbonate of iron	488
Fluor-spar	488
Sulphate of baryta	488
Clay and other silicates	489

COMPOSITION OF DIFFERENT KINDS OF LEAD.

	Page
Composition of different kinds of Lead, according to the analyses made in Laboratory of the Imperial Assay Office, Vienna	493
Do. made in the Royal Laboratory at Clausthal	494
Composition of German and Spanish Lead	495

COMMERCIAL DETAILS.

	Page
Purchase of Ores	496
Cost of Smelting in the Flintshire Furnace in Flintshire	496
List of British Lead-Smelters in 1870	497
Quantity of Lead Ore, Lead, and Silver, Produced in the United Kingdom in 1868	498
Summary for Five Years ending 1868	499
Production of Lead in various Foreign Countries	499
Quantity of Lead Imported into, and Exported from, the United Kingdom, in 1868 and 1869	499

MISCELLANEOUS DETAILS.

	Page
Cast Sheet-lead	500
Rolled or Milled Sheet-lead	501
Lead suitable for Pipes	506
Lead suitable for Sulphuric Acid Chambers	507
Lead suitable for Red-lead to be used in the Manufacture of Flint-glass	507
Lead suitable for White-lead	508

MANUFACTURE OF RED-LEAD.

	Page
History	508
General principles	509
Drossing-oven	509
Colouring-oven	511
Description of the process as conducted at the works of Messrs. Rawson, Barker, and Co., Sheffield	512
Do. as conducted by the Mining Company of Ireland at Ballycorus	514
Observations on Mr. Adkins' red-lead	516
Drossing by machinery	517
Mode of action of slag-lead in the process of drossing	517
Concentration of copper in the lead remaining unoxidized	519
Accidental production of red-lead	519
Concretionary matter in making red-lead	519
Poisonous effects of the manufacture of red-lead	520

EROSION AND PERFORATION OF LEAD BY INSECTS 521

POISONING BY LEAD.

Circumstances in which Poisoning by Lead is apt to occur	523
Symptoms of Poisoning by Lead	524
Course of the disease	525
Absorption of lead and its diffusion throughout the body	526
Treatment of Lead-Colic	526
Lead-Palsy	527
Preventive measures	527
Poisoning of Animals by Lead	530

APPENDIX.

Sulphide of Iron heated with Litharge	533
Reduction of Silicate of Lead by Iron	533
Sulphide of Lead heated with Oxide of Copper	534
Sulphide of Lead heated with Tin	535
Composition of the Crust formed on the exterior of a Lead-pipe	535
Additional results obtained in the Harz in Cordurié's process	535
On Lead-smelting in England in the 17th century	537
Composition of the Regulus obtained in smelting Australian Lead Ore	538
Table for computing from the percentage of silver the Troy weight of silver per statute ton	538

Index 539

ERRATA.

Page 23, line 5, *for* Winkelblec has *read* Winkelblech as.
„ 40, letter S dropped out of heading.
„ 41, line 18, *for* silicate *read* silica.
„ 122, line 35, *for* heat for *read* heat required for.
„ 124, 125, erase letters DD, F, A, in woodcut No. 8, and letters F, H in woodcut No. 10.
„ 203, line 27, *for* essays *read* assays.
„ 218, line 22, *for* lead-melting *read* lead-smelting.
„ 357, line 8, and page 405, line 6, *for* Niederschlagarbeit *read* Niederschlagsarbeit.

TO THE BINDER.

Coloured Diagram ..... *To face page* 135.

METALLURGY.

LEAD.

HISTORY.

The use of lead is recorded by the most ancient writers. Pliny designated the metal *plumbum nigrum* on account of its colour as compared with that of tin, which he termed *plumbum candidum*.[1]

PHYSICAL PROPERTIES OF LEAD.

Colour.—It belongs to the class of white metals, but has a decided blueish-grey tint. Lead-grey is an expression in common use to indicate kind of colour.

Lustre.—That of a freshly-cut surface is bright, but it soon becomes dull from atmospheric oxidation.

Crystalline system.—To the eye lead usually presents no sign of crystalline structure, though it is certain that the metal is an aggregation of crystals.[2] When a mass of molten lead is allowed slowly and partially to solidify without being disturbed, and the metal still liquid is poured off, the solidified portion will be found crystallized in skeleton octahedra of the cubical system, and somewhat similar in appearance to the fern-like crystals of chloride of ammonium deposited from an aqueous solution. I have pretty distinct solid octahedra, which I saw accidentally formed in the process of *quicking glass* as practised in Birmingham.[3]

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[1] Nat. Hist. Lib. 34. cap. 16, Sillig's edition, 1851, p. 189. See also Beckmann's History of Inventions, London, 1814, 4. p. 8.

[2] See Metallurgy, First Part, p. 4.

[3] The object of this process is the coating of glass with lead, whereby a bright reflecting surface may be obtained like that of an ordinary looking-glass. Small flat pieces of glass are painted over on one side with chalk or colcothar and water, and then left to dry. They are placed with the coated side downwards on the bottom of a flat tray of cast-iron, about a foot square, and surrounded with a vertical border of about 1 or 1½ inches, and are gradually heated in a large muffle to a temperature somewhat above the melting-point of lead. The tray is withdrawn, and melted lead is immediately poured into it sufficient to cover the glass, which is held down by pieces of wire. A slightly oscillating movement is given to the tray, so as to cause the molten lead to flow gently backwards and forwards. After a short time a plug is taken out of the corner of the tray, which is tilted to let the lead drain off as completely as possible. The pieces of glass will now be covered with a firmly-adherent film of lead; the adhesion is indeed so great, that a piece of quicked glass may be stamped under foot without detaching the lead. The crystals above mentioned

Ihle observed very distinct octahedral crystals of lead in a cavity in a pig of lead from the Muldener Hütte, Freiberg.[4] Although there can be little doubt that lead crystallizes in the cubical system, yet crystals sufficiently defined to admit of measurement by the goniometer do not seem to have been obtained.

Hardness.—Lead is the softest metal in common use. It may be easily cut with a knife and may be scratched even with the finger-nail; and it will make a grey streak on paper. It clogs an ordinary file, and can only be worked with the kind of file termed *rasp*, which presents numerous projecting points or burs formed by indenting the surface obliquely with a sharp-ended, three-sided punch. It is very feebly elastic or sonorous, and yields a remarkably dull sound when struck with a hard substance. This dulness of sound is generally proportionate to the purity of the lead. When lead is cast into the form of a hollow spherical or elliptical segment, it is stated to be very sonorous.[5] According to Lagerhjelm lead has only $\frac{1}{16}$ of the elasticity of wrought-iron.[6] It emits no sound or *cry*, like tin, on bending it backwards and forwards.

Malleability and ductility.—As might be inferred from its softness, lead is very malleable at ordinary temperatures, and may be rolled into thin sheets. It is also tough and easily flexible; and on bending even the cast metal no sound is emitted. By hammering it becomes harder, but acquires its original softness by annealing. Its ductility is not in the ratio of its malleability, and it cannot be drawn out into fine wire. Lead-wire of about $\frac{1}{16}$ inch in diameter is manufactured for gardeners, who sometimes use it in loops as a substitute for list in nailing trees to walls. When a pig of lead is heated to a certain degree bordering on its melting-point and then struck sharply with a heavy hammer, it breaks into pieces having a remarkable columnar structure, like tin similarly treated. The purer the lead the more largely columnar is its fracture. Interesting specimens illustrative of columnar fracture were sent by Messrs. Rawson, Barker and Co., of

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were produced when the lead had been accidentally left too long and had partially solidified. The lead employed should be of good quality, and in order to prevent it from becoming mixed with any oxide which may have formed on its surface, the tray is provided with the gutter-like arrangement shown in the annexed wood-cut. *a*, mouth, consisting of two vertical pieces of cast-iron, inclining towards each other, leaving only a slit for the passage of lead. *b*, a vertical partition of cast-iron extending nearly across the tray, further to aid in keeping the surface of the lead clean. *c*, hole for drawing off the lead. The tray is suspended at one end by a chain, and held by tongs at the other, whereby the oscillating movement before mentioned is easily given.

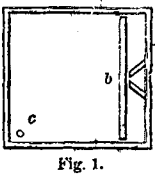

Fig. 1.

Quicked glass, coloured or uncoloured, is largely used for buttons. It is cut into small squares, and on the back of the lead coating of each a shank is soldered. The corners are ground off, and the circumference is cut and polished. I have seen quicked glass also applied in the construction of large mirrors, formed of small pieces of glass set in a concave frame. The glass-button maker, whom I have often watched at work with this process, told me that he prepared his lead by keeping it long melted under common salt.

[4] Berg. u. hüttenm. Zeitung, 1858, p. 123.

[5] Reaumur. The Chemical Works of Caspar Neumann, London, 1759, p. 54.

[6] Berzelius, Jahresb. 1829, 8. p. 78.

Sheffield, to the International Exhibition, 1862. The pigs of lead identical with those from which these specimens had been derived, and which had been proved by the analysis of Mr. Baker to be very pure, presented a highly crystalline surface. When heated to a certain degree, it may in the same manner as maccaroni be squeezed out into solid or hollow cylinders. Solid cylinders or rods of lead are thus made for the manufacture of rifle bullets, as at the Royal Arsenal; and hollow cylinders or pipes are also largely made by the same process, instead of the old one of drawing out cold from short lengths cast hollow. We have a beautiful specimen of what might be designated "lead moss," which consists of a fine hair-like mass. It was found on the outside of a Pattinson desilverization pot filled with lead which had been left to solidify in the pot, and resulted from the liquid lead having been forced through a minute hole in the pot. The moss was apparently composed of a single continuous thread, twisted and folded upon itself.

Specific gravity.—Berzelius adopted 11·445 as the specific gravity of pure lead, but it is not stated whether this number was deduced from his own experiments or those of others.[7] It is now considered as too high. Kupffer obtained the following results:—[8]

Sp. gr. at 17° C.	11·3303	or, reduced to 0° C.	11·3468
,, 15° C.	11·3299	,, ...	11·3445
,, 14° C.	11·3338	,, ...	11·3484

Reich of Freiberg, found the specific gravity of pure lead to be 11·370 at 0° C., that of water at 4° C. being taken as unity.[9] Streng, of Clausthal, determined the specific gravity of what he terms "the purest Pattinsonized lead," but what in England would be regarded as impure; and from three experiments at 4° C. deduced the mean 11·395, which, calculated for 0° C., would be 11·386. But this lead contained from 0·015% to 0·02% of copper, and from 0·02% to 0·04% of antimony.[1] According to Matthiessen's determination the specific gravity of lead is 11·376 at 14° C.[2] The specific gravity of extraordinarily pure lead prepared by Mr. Dick in quantity has been determined in my laboratory by Mr. Tookey and found to be as under at 60° Fahr. = 15·5° C.:—

Melted under cyanide of potassium	11·358
The same piece hammered	11·387
A piece chiselled out from the pig	11·382

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[7] Traité de Chimie, 1846, 2. p. 576.

[8] Berg. u. hüttenm. Zeit. 1860, p. 125.

[9] Ibid. Reich employs the following formula for computing the specific gravity at 0° C.:—

$$\alpha = R^3 (\gamma q - (q - 1)\alpha)$$

α = required specific gravity, γ = sp. gr. of water at $t°$ C. (sp. gr. of water at + 4° C. = 1), α = sp. gr. of air (in relation to that of water) on the average about = 0·0012, q = uncorrected sp. gr. of the body, R^3 the volume of lead at $t°$ C. (that at 0° C. being = 1). The linear dilatation of lead from 0° C. to 100° C. being taken as = 0·00285, its cubical dilatation is

$$R^3 = 1 + \frac{3 \times 0{\cdot}00285 \times t}{100}$$

the true sp. gr. of lead at $t°$ C., or

$$e = \gamma q - (q - 1)\alpha.$$

In the determination of the specific gravity the temperature of the water and the air is supposed to be the same.

[1] Ibid.

[2] Kopp u. Will, Jahresb. 1860. p. 112.

Reich observed that by rolling into thin sheet the specific gravity of lead was increased from 11·354 to 11·365.[3]

C. Sainte-Claire Deville states that the specific gravity of lead very slowly cooled and crystalline is 11·254, while that of the same lead cooled rapidly after fusion by pouring into water is 11·363.[4]

The specific gravity of lead is diminished by the presence in sensible proportion of any of the substances which constitute the usual impurities in commercial varieties of the metal; so that, other things being equal, the greater the purity the higher the specific gravity of lead.

Resistance to pressure.—Coriolis, a French engineer, has experimented on this subject and published the following results.[5] His object was to ascertain whether lead might be used to determine heavy weights by the degree in which it is crushed under pressure, and whether on this principle a simple machine might be constructed as a substitute for the machine in common use for weighing vehicles, such as carts and carriages. He proposed to subject pieces of lead of uniform dimensions in the case of two-wheeled vehicles to the pressure caused by the passage of one wheel only which would represent half the total weight of the vehicle. The difficulty of obtaining pieces of lead very homogeneous, and the too great influence of the duration of the pressure upon the degree of crushing, shewed the scheme to be impracticable. Nevertheless, the results at which Coriolis arrived are of permanent value.

The pieces of lead operated upon were cylinders 24 millimetres (0·96 inch) in diameter and 19 millimetres (0·76 inch) in thickness, each weighing from 100 to 101 grammes (0·2205 lb. to 0·227 lb.). The scale employed for measuring the thicknesses was divided into 680 parts, so that each division corresponded to the 36th of a millimetre. The lead to be crushed was put between two plates of iron forming a kind of box, in which it might extend laterally under pressure. The cover of this box carried a steel button upon which the wheel should rest. The wheel was raised or lowered by a jack which could be easily worked.

The chief conditions to be investigated were the nature of the lead, its temperature, the time of the pressure, the method of bringing the weight to be borne upon the box, and the state of the surfaces of the plates of iron between which the crushing was effected. It was not possible to separate these different influences, except that relating to the nature of the lead. In order to eliminate the influence of the duration of the pressure of the wheel upon the lead, the wheel was to be allowed to remain upon the box only one minute, measured very exactly from the moment when the jack ceased to support the axle-tree to the moment when it began to be raised.

In order to prove that in the movement of descent upon the box

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[3] Kopp u. Will, Jahresb. 1859. p. 201.
[4] Liebig u. Kopp, Jahresb. 1855, p. 15.
[5] Expériences sur la résistance du Plomb à l'écrasement, et sur l'influence qu'a sur sa dureté une quantité inappréciable d'oxide. Par M. G. Coriolis, ingénieur. Ann. de Chim. et de Phys. 1830, 44. p. 103.

there was no shock which might interfere too much with the results, a piece of lead which had been crushed during one minute under a charge of 1500 kilogrammes (3307·5 lbs.), and which had been reduced from its original thickness of 680 to 459 divisions of the scale, was replaced under the wheel during two minutes, whereby it was further reduced to 418. Another piece of lead, which, under the same charge during one minute, had been reduced to 462, was replaced in the box and left during two minutes, but at eight times successively during a quarter of a minute each; and after this treatment, in which it had been exposed seven times oftener to the *vis viva* of the descent than in the case of the first piece, it was reduced only to 399, or on the average to about 3 divisions of the scale at each shock. Similar experiments were several times repeated with the heaviest charges ever to be sustained, and with not greater differences between the results. The conclusion to which Coriolis came was, that the differences between the lighter and heavier shocks within the limits of the precautions easy to be taken were not comparable with those due to the nature of the metal and the mode in which it was melted previously to pouring into the mould. Experiments were made upon pieces of lead heated to 20° C. or 30° C. as well as cooled to 0° C., and no difference was found which might not have been caused by that of the nature of the metal. Indeed, Coriolis remarks, it is easy to conceive that temperature should have but little influence, when it is remembered that the crushing of itself developes so much heat that the lead can hardly be touched after it has just been compressed; and that, consequently, this heat ought to lessen the effect of the original temperature. It was found that, whether the surfaces of the box which came in contact with the lead had been filed, or allowed to become somewhat rusty, or in other words, whether they were more or less polished or rough, the result was such as might be explained by the nature of the lead.

In all the succeeding experiments, except when otherwise stated, the duration of the pressure was one minute.

1. Commercial pig-lead (variety not specified) cast without precautions against oxidation. Charge of 1500 kil. (3307·5 lbs.). In twelve experiments the mean reduction in thickness of the lead was from 680 to 503, the extremes being 465 and 546.

2. Mint assay-lead, cast without precautions against oxidation. Charge of 1500 kil. (3307·5 lbs.). In six experiments the mean reduction in thickness of the lead was from 680 to 463, the extremes being 459 and 471.

The same lead. Charge of 1824 kil. (4021·9 lbs.). In three experiments, the mean reduction in the thickness of the lead was from 680 to 336, the extremes being 335 and 337.

The same lead. Charge of 1950 kil. (4299·7 lbs.). In five experiments the mean reduction in thickness of the lead was from 680 to 337, the extremes being 331 and 341.

The same lead. Charge of 3175 kil. (7000·9 lbs.). In eight experiments the mean reduction in thickness of the lead was from 680 to 296, the extremes being 292 and 303.

The same lead after having been re-melted and mixed with more oxide than in the foregoing experiments. Charge of 1500 kil. (3307·5 lbs.). In seven experiments the mean reduction in thickness of the lead was from 680 to 490, the extremes being 487 and 495.

The same lead as the last under different charges.

1564 kil. (3448·6 lbs.)	Thickness after crushing	485
1596 ,, (3519·2 lbs.)	,, ...	477
1688 ,, (3722·0 lbs.)	,, ...	471

3. Lead reduced from its carbonate and melted once under deoxidizing agents, such as tallow or colophany (commonly known as *rosin*).

Charge of 1950 kil. (4299·7 lbs.). In six experiments the mean reduction in thickness of the lead was from 680 to 333, the extremes being 322 and 341.

The same lead melted a second time and containing more oxide (mechanically mixed?) than that in the last experiment. Charge the same. In eleven experiments the mean reduction in thickness of the lead was from 680 to 351, the extremes being 341 and 363.

The same lead melted a third time and containing, it is alleged, a little more oxide. Charge the same. In eleven experiments the mean reduction in thickness of the lead was from 680 to 398, the extremes being 365 and 419.

Thus, in spite of the use of deoxidizing agents, the lead increased in hardness at each fresh melting.

4. Lead reduced from its carbonate and cast so as to prevent oxidation by the air.

The lead was melted under a thick layer of powdered charcoal, in crucibles having at the bottom copper-stops through which only the metal below the surface might flow into the mould. [The lead would thereby become alloyed with a little copper.] The molten lead was also stirred with wood in order to bring up to the surface any intermixed oxide, and at the same time with a view to promote deoxidation. In order to ascertain whether the temperature of the metal at the time of casting had any effect upon its hardness, at each casting half the number of pieces were poured at a cherry-red heat into the mould, and the other half at the lowest possible temperature.

Charge of 1760 kil. (3880·8 lbs.). In twelve experiments the mean reduction in thickness of the lead was from 680 to 303, the extremes being 290 and 314.

The same lead melted a second time. Charge the same. In fifteen experiments the mean reduction in thickness of the lead was 311, the extremes being 295 and 321.

The same lead melted a third time. Charge the same. In eight experiments the mean reduction in thickness of the lead was 301, the extremes being 295 and 315.

The lead of half the number of pieces in each of this series of experiments (4) was poured red-hot into the mould, but no sensible difference was caused by casting at this temperature.

It will be observed that the pure lead (from carbonate), melted under charcoal and tapped from the bottom of the crucible, was reduced to a mean thickness of 303 under the charge of 1760 kil. (3880·8 lbs.); the same kind of lead, which had not been kept constantly covered during fusion and had been poured into the mould in the usual way, was reduced to a mean thickness of 333 under the charge of 1950 kil. (4299·7 lbs.), a charge which, in the case of lead like the other, ought to have caused a reduction in thickness only to about 283. This statement, showing that lead cast under cover from the air is the most compressible, requires confirmation.

5. Influence of the duration of the pressure. Pure lead (from carbonate) cast a second time, without being covered, and which was mixed with a little oxide. Charge of 1500 kil. (3307·5 lbs.).

Duration of pressure in seconds.	Reduction of volume from 630.	Duration of pressure in seconds.	Reduction of volume from 630.
5	506	40	497
10	503	45	491
15	502	50	487
20	498	55	483
25	501	60	485[6]
30	501	65	483
35	499	75	483

Pure lead (from carbonate) once cast without being covered, and mixed with a little oxide. Charge of 1950 kil. (4299·7 lbs.).

Duration of pressure in seconds.	Reduction of volume from 630.	Duration of pressure in seconds.	Reduction of volume from 630.
30	365	75	321
45	331	90	319
60	322	120	313

Pure lead (from carbonate) cast a second time without being covered. Charge of 1950 kil. (4299·7 lbs.).

Duration of pressure.	Reduction of volume from 630.
60 seconds	355
16 minutes	299

Pure lead (from carbonate), once cast under cover. Charge of 1760 kil. (3880·8 lbs.).

Duration of pressure.	Reduction of volume from 630.
1 minute	317
1 hour	245
24 hours	223

Thus after an hour under the same weight, the lead had not reached a state of stability. The question as to the presence of oxide of lead in metallic lead melted with access of air will be hereafter examined.

Tenacity.—Lead-wire of about $0^{mm}3$ (0·12 inch) in diameter breaks under a weight of 14·75 kilogrammes (32·52 lbs.).[7] Berthier states

[6] This is probably an error and should be 483.

[7] Berzelius, Traité de Chim. 1846, 2. p. 576.

that lead-wire of 0^{mm} 2 (0·08 inch) in diameter breaks under a weight of 9 kil. (19·8045 lbs.).[8] Baudrimont states that lead-wire 1^{mm} 8755 (0·075 inch) in diameter breaks in a few seconds under a weight of 6·5 kilogrammes (14·3325 lbs.).[9] Wire of pure lead elongates considerably before it breaks: thus Karmarsch found lead-wire 16⅓ inches long and 0·061 inch in diameter extended to 81½ inches before it broke;[1] but in this case obviously much will depend upon the *time* during which rupture is effected. Wertheim obtained the following results. The lead operated upon was reduced from oxide, prepared by the calcination of pure nitrate of lead. The tenacity is estimated in kilogrammes per square millimetre of sectional area.[2]

	Rupture slow.	Rupture sudden.	At 100° C.
	Between 15° and 20° C.		
Lead cast	1·25	2·21	
,, drawn out...	2·07	2·36	
,, annealed ...	1·80	2 04	0·54

Specific heat.—According to Regnault, between 10° C. and 100° C. it is 0·03140, but between −77°75 C. and 10° C. it is 0·03065.[3] For molten lead between 350° C. and 450° C. Person found it to be 0·0402.[4]

Dilatation by heat.—Calvert and Johnson give 0·00003005 as the coefficient of linear dilatation for 1° C. between 0° C. and 100° C.[5] According to Kopp, the coefficient of cubical dilatation for 1° C. is 0·000089.[6]

Melting-point.—Lead, as every one knows, is easily fusible. Rudberg assigns 326° C. as the melting-point of lead.[7] Measured by the mercurial thermometer, Person found it to be 334° C., which by Regnault's table would indicate 326°2 C. by the air-thermometer.[8] The results of other observers as to the melting-point of lead differ considerably from each other, the extremes being 262° C. (Biot) and 334° C. (Kupffer).[9] Dalton accepted the number 322° C. (= 612° F.).[10] Solid lead immediately sinks in molten lead of the same kind.

Latent heat.—It was found by Person to be 5·369, *i.e.* one part by weight of lead on solidification evolves heat sufficient to raise 5·369 parts of water 1° C.[1]

Conductivity for heat and electricity.—According to Wiedemann and Franz, the conductivity of silver for each being taken at 100, that of lead for heat is 8·5 at 12° C. and for electricity 10·7.[2] By Matthiessen's

[8] Traité des Essais, 1834, 2. p. 662.
[9] Baudrimont, Traité de Chimie, 1846, 2. p. 179.
[1] Berzelius, Jahresb. 15. p. 131.
[2] Ann. de Chim. et de Phys. 3. s. 12. p. 409.
[3] Ibid. 3. s. 1849, 26. p. 273.
[4] Ibid. 3. s. 1848, 24. p. 136.
[5] Brit. Assoc. Rep. 1858 (28th meeting), p. 46.
[6] Liebig u. Kopp, Jahresb. 1851, p. 55.
[7] Ibid. 1847, p. 71.
[8] Ann. de Chim. et de Phys. 3. s. 1848, 24. p. 136.
[9] Gmelin, Handbuch, Trans. 5. p. 107.
[10] A New System of Chemical Philosophy, 1808, Part I. p. 248.
[1] Ann. de Chim. et de Phys. 3. s. 1848, 24. p. 136.
[2] Jamin, Cours de Physique, 1859, 2. p. 333.

determination the electric conductivity of lead is 7·77 at 17°3 C.[3] E. Becquerel found it to be 8·245 between 12° C. and 13° C.; he experimented upon two lead-wires of 0^{mm} 687 and 0^{mm} 858 in diameter respectively, in the state in which they left the draw-plate. The coefficient of resistance for 1° C. between 10°3 and 98° C. was 0·004349.[4]

Volatilization.—With access of air fumes of oxide of lead are evolved at a bright red-heat; but without access of air lead is not sensibly volatilized below a white-heat. It boils rapidly before the oxyhydrogen blowpipe. It cannot, however, be distilled like zinc *per se* in close vessels. However, in the extraction of zinc from ores containing lead, the vapour of the zinc is mixed with the vapour of lead. According to Berthier, lead heated in a brasqued crucible to about 50° (Wedgwood's pyrometer) loses 0·5% of its weight and 9% at 150°.[5] In the processes of smelting and cupelling lead there is considerable evaporation of the metal or of its compounds. When lead is heated to the temperature at which it begins to fume and oxidize rapidly, it gives off a well-marked odour. The same odour is perceived when finely-divided litharge (PbO) is shaken in a room, so that a trace of it becomes diffused in the air. At a high temperature in contact with air it burns with a livid flame.

Other physical properties.—Lead is tasteless, but emits a characteristic odour when rubbed between the fingers.

When two plane and perfectly clean surfaces of lead, such as may be easily produced by cutting the metal with a sharp knife, are pressed together, they adhere with great tenacity. This is a well-known fact, even to schoolboys, who usually perform the experiment by dividing a leaden bullet through the centre with a pocket-knife and then pressing the halves together on their cut surfaces with a twisting or screwing movement. Adhesion may be similarly effected between tin and lead by passing superimposed ingots of these metals through the rolls, and for the discovery and application of this fact Dobbs obtained a patent in 1805. This kind of cohesion is, I think, correctly regarded by Fournet as true welding, and as dependent upon the softness of the metal at ordinary temperatures.[6] With iron the requisite softness is induced only at a very high temperature. The effect, however, is essentially the same in this case of the cohesion of lead and in the welding of iron. In the case of iron heat acts simply by inducing that necessary quality of softness which exists in lead at ordinary temperatures.

Lead in a state of fine division may by mere pressure be made into a solid mass, as shewn by the following experiment of Bolley. A paste of sulphate of lead (PbO,SO^3) and water is spread an inch thick upon a plate of zinc, and the whole is plunged into the upper part of a solution of common salt (NaCl) not quite saturated. After a few days the paste will be changed into a coherent soft mass of lead (*Blei-*

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[3] Phil. Mag. 1858, 4. s. 16. p. 219.
[4] Ann. de Chim. et de Phys. 1846, 3. s. 17. p. 254.
[5] Traité des Essais, 2. p. 662.
[6] Ann. de Chim. et de Phys. 1840, 75. p. 435.

schwamm), which by immersion in hot water may be freed from the interposed solution of salt. Under a powerful press this mass becomes a solid plate of flexible lead, which, stamped in a mould, gives a sharp impression. If not strongly pressed, the mass readily oxidizes.[7]

CHEMICAL PROPERTIES OF LEAD.

Atomic weight.—Pb. 103·572 Berzelius. 103·453 and 103·460, as found by different methods, Stas.[8] 103·52, Marignac.[9]

LEAD AND OXYGEN.

Lead in a compact state suffers no change in perfectly dry oxygen or dry air at ordinary atmospheric temperatures; but in moist oxygen or moist air it becomes tarnished by the formation of a superficial coat of oxide. In an atmosphere saturated with aqueous vapour this oxidation takes place in a few days, and the bright surface of the metal before it becomes dull grey presents in succession all the colours of the rainbow. The action is promoted by a gentle heat.[10]

When lead is kept exposed to the air below but near its melting-point, its surface becomes covered with a grey powder, supposed by Berzelius to be sub-oxide. At the temperature of its melting-point a higher yellow oxide (PbO) is formed, which afterwards gradually passes into red-lead (Pb^3O^4). The surface of the metal after fusion becomes beautifully iridescent, and superficial films thus coloured may be removed and permanently preserved. At a bright red-heat oxidation proceeds rapidly, and the resulting oxide is molten at that temperature. In order to convert a mass of lead into oxide it is necessary to keep the air constantly acting upon the metal by agitation or otherwise. Much heat is evolved during the oxidation; for on exposing metallic lead and oxide to the same temperature, the oxide produced upon the former may be as liquid as oil, while the latter is scarcely softened.[1]

Lead is readily dissolved by nitric acid, which when somewhat diluted is the best solvent of the metal. It is slowly dissolved by long boiling in hydrochloric acid, hydrogen being disengaged. It is not acted upon by dilute sulphuric acid, but is converted by the concentrated boiling acid into sulphate of lead, with the production of sulphurous acid. Acetic dissolves it only in contact with air.

According to Stolba, when lead is exposed to the action of boiling water, hydrogen is evolved and a solution of lead is produced which has an alkaline reaction.[2] Dr. Beck, of Darmstadt, experimented upon this subject in my laboratory, and arrived at the conclusion that pure boiling water, perfectly free from atmospheric air, has no action upon lead. If, however, atmospheric air has access to the water during the experiment, or if the water has not been previously

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[7] Liebig u. Kopp, Jahresb. 1849, p. 278.
[8] Kopp u. Will, Jahresb. 1860, p. 4.
[9] Ibid. 1858, p. 185.
[10] Bonsdorff, Sur l'oxidation des métaux dans l'air atmosphérique. Répertoire de Chimie, 1838, 3. p. 42.

[1] Dumas, Traité de Chimie appliquée aux Arts, 1831, 2. p. 539.
[2] Stolba, Journ. f. prakt. Chemie, 1865. Quarterly Journ. of Science, No. 7, July 1865, p. 457.

completely deprived of atmospheric air, the lead is acted upon, and the presence of the metal may in that case be detected in the water. Dr. Beck also found that neither commercial lead,—lead containing 2% of antimony,—an alloy composed of 90% of lead, 5% of antimony, and 5% of zinc,—nor an alloy composed of 95% of lead and 5% of zinc, was acted upon by pure boiling water perfectly freed from atmospheric air. The alloy containing 2% of antimony was but little acted upon by water with access of atmospheric air, the cut surfaces of the metal continuing bright after remaining in contact with water and atmospheric air during several days.

Lead is very readily and quickly thrown down in the metallic state by zinc and cadmium from the solution of its nitrate.[3]

Dioxide or Suboxide of Lead.

Pb^2O.—It is this oxide which, according to Berzelius, is produced by the action of moist oxygen at ordinary temperatures, and when lead is heated in contact with the air below, yet near, its melting-point.[4] Thus made, it has a dark-grey colour. The existence of such an oxide has been denied, and the substance prepared as above described has been regarded merely as a mixture of protoxide and finely-divided metallic lead. A definite dioxide may be prepared by heating oxalate of lead in a retort at, but not above, 300° C. Care must be taken to prevent access of air after the evolution of gas ceases and during subsequent cooling. The reaction is thus expressed:—$2\,(PbO,C^2O^3) = Pb^2O + CO + 3CO^2$.

The product is described as very dark-grey or dull velvety-black, and perfectly homogeneous. Mercury when triturated with it under water does not extract any lead from it. No lead is dissolved out of it by boiling with a solution of sugar. By dilute as well as strong acids it is resolved immediately into protoxide of lead which combines with the acid and into grey flocks of metallic lead, which by compression acquire a metallic lustre. It is also similarly resolved by the action of a solution of caustic potash or soda. Heated to redness in a close vessel, it is changed into metallic lead and protoxide of lead, which is greenish from admixture with some of the finely-divided metal. Heated at one point in the air it takes fire and continues to burn like tinder until it is wholly converted into protoxide. When moistened with a little water and exposed to the air, it begins after a few seconds to become heated, owing to the absorption of oxygen, and is finally changed into hydrated protoxide.[5] It cannot certainly be inferred from the foregoing data that the substance causing the tarnish of lead and that formed by heating the metal below its melting-point with access of air are identical with the dioxide from oxalate of lead.

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[3] Das Verhältniss der chem. Verwandtschaft zur galvanischen Elektricität. N. W. Fischer, Berlin, 1830. 137.

[4] Traité de Chim. 2. p. 577.

[5] This oxide has been especially investigated by Dulong, Boussingault, and Pelouze. See Berzelius, Jahresb. 15. p. 156; Ibid. 22. p. 122.

Protoxide of Lead.

PbO.—It occurs amorphous as well as distinctly crystallized. It varies somewhat in colour with the mode of its preparation. It is made on the large scale by keeping lead freely exposed to the air at a temperature considerably higher than the melting-point of the metal, but lower than that of the protoxide, when it is obtained in the state of yellow powder termed *massicot*. On the small scale it may be procured in the state of fine sulphur-yellow powder by heating sub-nitrate,[6] carbonate, or oxalate of lead to a degree sufficient to decompose those salts, but not to fuse the oxide. By trituration this powder acquires a red tint.[7] Protoxide of lead melts at a good red-heat, and on solidification becomes a crystalline mass, which is known as *litharge*, a word derived from the Greek and meaning literally *silver-stone* (ἄργυρος, silver, and λίθος, stone). It is so named from the fact of its production in the process of refining silver by lead. Litharge is occasionally met with in measurable crystals, and Hausmann and Mitscherlich describe rhombic octahedrons of litharge.[8] Grailich examined fine transparent sulphur-yellow scales from smelting works in the Harz, and found them to be rhombic with angles of 97° and 83°; their specific gravity was 8·02.[9] Rammelsberg measured small green transparent crystals of litharge from the "Ofenbruch" of the Königshütte furnaces, Upper Silesia, and pronounces them to belong to the pyramidal system (*viergliedrig*).[10] I have seen beautiful crystalline plates of protoxide of lead in the cavity of a cupel, which, after the completion of an assay of argentiferous lead, had been accidentally left to cool in the muffle. Under the *tests* of silver-refining furnaces may be seen masses of highly crystalline litharge depending like stalactites. The colour of protoxide of lead is either yellow or reddish-yellow, according as it is cooled rapidly or slowly after fusion. The yellow oxide becomes brown-red when heated to a certain degree, but acquires its original colour on cooling. The red variety is stated to be specifically lighter than the yellow.[1]

The following observations on the colours of litharge have been made by a friend of mine who has had great experience in the manufacture of that substance. Litharge when reduced to fine powder has a buff colour; but according to its state of aggregation, it has other colours, all of which are changed to buff by grinding. It will be borne in mind that the question here is of the colour of pure litharge, irrespective of the colouring effect of foreign matters. Heated to dull redness, buff-coloured litharge passes through various shades of red and purple; it agglutinates somewhat and shrinks a little in bulk; and it cools to a

[6] In order to obtain the oxide perfectly pure special precautions must be taken. When nitrate of lead is decomposed by heat in a platinum crucible, this is always attacked, though only in a slight degree. By the use of a gold crucible this difficulty would probably be obviated. See Berzelius, op. cit.

[7] Berzelius, Traité de Chim. 2. p. 579.

[8] Leonhard, Hütten-Erzeugnisse, 1858, p. 353. Studien des Götting'schen Vereins Bergmännischer Freunde, 1856. 7. 65.

[9] Kopp u. Will, Jahresb. 1858, p. 186.

[10] Handbuch der Kristallographischen Chemie, 1855, p. 30.

[1] Leblanc, Gmelin's Handbook, 5. p. 109.

lemon-yellow powder, which is not so fine as before heating. When this yellow powder is ground, it is buff-coloured as at first. These changes in condition and colour may be repeated indefinitely. Litharge, which has been heated sufficiently to render it yellow on cooling, is, in technical language, "burnt;" and in this state it cannot be made into red-lead without re-grinding, at least not under the ordinary conditions of a red-lead oven.

If litharge is melted in quantity and allowed to run in a fine stream on cold iron, it solidifies to a lemon-yellow cake, which, if not touched, may be kept unchanged; but which, if ground, becomes buff. When molten litharge is allowed to run in quantity into a large ladle and left to cool slowly therein, it can be turned out in a lump when the temperature is reduced to dull redness. In the course of a few hours the lump will have cooled and in great part fallen to powder, or rather to scales, termed "flake litharge;" and during cooling it is interesting to observe how it swells and exfoliates. The litharge at the upper surface and in contact with the ladle, never falls completely to flakes, because it cools too quickly; it is termed "coarse litharge," as in the process of sifting it remains upon the screen, through which the flake litharge passes. It has the same colour as litharge which after fusion has been suddenly cooled. Flake litharge has a reddish-golden yellow colour, which, together with its lustre, is suggestive of bisulphide of tin in the well-known form of *mosaic gold*. Both kinds of litharge, coarse and flake, are buff-coloured when ground, and each variety may be converted into the other by re-melting and cooling under the conditions above stated. Coarse litharge, when heated in a lump to dull redness, does not change in colour as flake litharge does, which, after having been thus heated, has a lemon-yellow colour when cold, and after subsequent grinding a buff colour.

When red- or orange-lead is heated sufficiently to be decomposed, the product is a lemon-yellow powder, which on grinding becomes buff-coloured. The same occurs with carbonate of lead, when heated a little above the temperature at which it would be converted into orange-lead.

Protoxide of lead may also be obtained crystallized by various *wet* methods. A strong solution of caustic potash boiled with protoxide of lead to saturation, deposits as it cools part of the oxide, and that in yellow scales resembling litharge. If the solution is not saturated, it is only after cooling that any oxide is deposited; and then it separates at first in yellow scales, and afterwards in red scales. These yellow and red scales have the same composition; and the latter become yellow after having been heated and cooled. According to Mitscherlich the red variety of protoxide may also be prepared by pouring a concentrated solution of a salt of lead into a boiling pasty mixture of hydrate of lime and water, and keeping the whole boiling until the precipitated oxide of lead be changed into a heavy red powder, from which, after cooling, the intermixed hydrate of lime in excess may be easily removed by levigation.[2] Fremy says that by evaporating an alkaline solution of

[2] Berzelius, Traité de Chim. 2. p. 580.

protoxide of lead, the latter is deposited in anhydrous olive-brown crystals, which by calcination acquire a fine yellow colour without losing weight. He further affirms that friction alone suffices to communicate the colour of massicot to anhydrous protoxide of lead.[3] Calvert states that rose-red and nearly cubical (?) crystals are formed on the cooling of a solution of caustic soda, of a specific gravity ranging from 1·375 to 1·442, and saturated hot with protoxide of lead. This observer also states that the powder of protoxide of lead thrown into molten hydrate of soda becomes instantly almost as red as minium, and retains this colour when cold. The powder of this red variety of protoxide of lead, which is said to be amorphous, is yellow like that of litharge; and the red crystals of Calvert, after exposure to a red-heat, become yellow on cooling without changing in crystalline form.[4] Becquerel states that he obtained crystals of protoxide of lead similar in lustre to those of litharge resulting from fusion, by keeping peroxide of lead (PbO^2) for some time in molten hydrate of potash, and washing the cold product with water so as to remove the alkali; he adds that crystals of peroxide of lead were also formed.[5]

Protoxide of lead also occurs in colourless crystals. Mitscherlich procured such crystals by dissolving as much protoxide of lead as possible in a hot dilute solution of caustic potash, and afterwards leaving the solution at rest.[6] Colonel Yorke observed adherent to the surface of lead, which had been exposed to the joint action of air and water, minute colourless, semi-transparent crystals of anhydrous protoxide of lead, with very brilliant facets, and having the form of rhombic dodecahedrons with the acute angles replaced by tangent planes. When heated, these crystals became opaque and orange-coloured, but without losing their form or brilliancy.[7] I have received from Colonel Yorke specimens of these crystals. By the following process Payen got anhydrous protoxide of lead in distinct rhombic tables: 100 parts by measure of a saturated solution of tribasic acetate of lead were mixed with 50 of water, and the whole was heated to the boiling-point. On the other hand, 50 parts by measure of water heated to 80° C., and then mixed with 8 of ammonia-water were added to the first solution contained in a vessel immersed in a water-bath at 100° C. In about a minute, brilliant scales were seen to group themselves on the sides and at the surface of the solution. In about half an hour they became numerous, adhering to the sides of the vessel in plume-like clusters (*aigrettes*) of a bright lustre. The colour of the crystalline deposit was yellow, and somewhat deeper in colour than that previously obtained at a lower temperature and with other proportions of the solutions. Payen recommends this experiment as well adapted for lecture illustration. Under different conditions as to dilution and temperature, crystallized hydrate of protoxide of lead was deposited along with the anhydrous oxide.[8] Becquerel has described the forma-

[3] Ann. de Chim. et de Phys. 1844, 12. p. 489.
[4] Berzelius, Traité de Chim. 2. p. 581.
[5] Traité d'Électricité et de Magnétisme, 1855, 2. p. 129.
[6] Berzelius, Traité de Chim. 2. p. 580.
[7] Phil. Mag. 1834, 5. p. 83.
[8] Ann. de Chim. et de Phys. 1837, 66. p. 52.

tion of protoxide of lead in very limpid dodecahedral crystals with pentagonal faces, on the surface of a sheet of lead which had been kept in a hermetically sealed glass tube containing a not very dilute aqueous solution of acetate of lead and litharge in powder.[9] According to Mitscherlich, protoxide of lead crystallizes in the same system whether produced in the *dry* or *wet* way.

Protoxide of lead, as has been previously stated, melts at a good red-heat, and while molten is transparent and orange-coloured. According to Fournet, it volatilizes at a white-heat, but less easily than metallic lead.[1] It solidifies with expansion into a reddish-yellow crystalline, but not vitreous, mass, unless it contains silica in combination.[2] It is talc-like to the touch, and so soft that it may be scratched with the finger-nail and easily cut. It may be easily divided into crystalline scales. When molten it powerfully corrodes earthen crucibles; and if they are coarse-grained rapidly permeates them.

Berzelius, without doubt erroneously, states that protoxide of lead above its melting-point is partially reduced with the separation of metallic lead, which collects at the bottom of the vessel; and he adds that this happens especially when the oxide is melted "at a very high temperature in crucibles of silver or platinum." From the first part of this sentence it might be inferred that reduction takes place *per se;* and from the second by the action of the silver or platinum. The term "very high temperature," seems inapplicable in the case of silver crucibles, as silver fuses at a good red-heat.[3]

Protoxide of lead is quickly and completely reduced at a dull red-heat, and even at a lower temperature, by charcoal, coke, or coal; and by carbonic oxide, hydrogen, and cyanogen. The temperature at which reduction occurs is below that at which carbonic acid is converted into carbonic oxide by contact with any of the above-mentioned solid carbonaceous matters; so that when these agents of reduction are employed carbonic acid, and not carbonic oxide, is the product evolved. Winkelblech states, that the crystalline oxide of lead made by the addition of potash to a hot solution of acetate (sugar) of lead, is reduced by carbonic oxide or hydrogen at a temperature not much above 100° C.[4] It is reduced on the large scale in furnaces, as will be hereafter described. It is reduced when heated with iron, zinc, copper, tin, antimony, and various other metals. Details on this subject will be given further on under the head of "Oxidizing action of Litharge."

Molten protoxide of lead conducts electricity.[5]

Protoxide of lead prepared from the decomposition of nitrate of lead by heat dissolves, according to Bonsdorff, in about 7000 times, and according to Yorke in about 12,000[6] its weight of water, and the solution

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[9] Traité d'Électricité et de Magnétisme, 1855, 2. p. 129.

[1] Ann. de Chim. 55. p. 414.

[2] Breivend, Gmelin's Handbook, 5. p. 111. Quoted from Journ. f. prakt. Chemie, 23. p. 250.

[3] Berzelius, Traité de Chim. 1846, 2. p. 581.

[4] Gmelin, Handbook, 5. p. 112.

[5] Faraday, Experimental Researches in Electricity, 1839, p. 234.

[6] Phil. Mag. 1834, 5. 5. p. 94.

has an alkaline reaction ;[7] but Bineau asserts that after fusion, *i.e.* in the state of litharge, it is quite insoluble in water.[8] This aqueous solution of protoxide of lead decomposes solutions of alkaline sulphates, nitrates, phosphates, chromates, oxalates, carbonates, and haloid salts (chlorides, &c.). At least $1\frac{1}{2}$ equivalent of the protoxide is required for the separation of 1 equivalent of alkali.[9] The solution, Bonsdorff says, is so sensitive in the detection of carbonic acid, that on exposure to atmospheric air it immediately becomes turbid, and lets fall a precipitate of hydrated carbonate of lead. On the other hand, Siebold and Brendecke affirm that protoxide of lead, however prepared, is perfectly insoluble in pure water, as well as water containing salts in solution, and whether air be excluded or not; but in the last case a carbonate of lead may be formed, which, if not carefully separated by filtration, may occasion turbidity.[1]

Litharge was melted, and when cold was ground fine and boiled for about 15 minutes with distilled water, which had been previously boiled for half an hour in order to expel air. The filtered water immediately turned red litmus-paper blue. Massicot was treated in the same manner and gave the same result. (J. C. Cloud, in my laboratory.)

Protoxide of lead is a powerful base, and exists in an extensive series of salts, of which many are basic. It also acts the part of an acid towards strong bases such as potash, soda, baryta, and lime. One part of protoxide of lead dissolves in a concentrated solution containing 11 parts of caustic potash or 13 parts of soda. The liquid obtained by boiling milk of lime with protoxide of lead blackens hair, nails, horn, and wool, owing to the formation of sulphide of lead at the expense of the sulphur in those animal substances.

Wöhler has described a compound of oxide of silver and protoxide of lead of the formula $AgO+2PbO$. By the addition of caustic potash to a solution of a salt of lead containing a salt of silver, a yellow precipitate is formed which is the compound in question, and which, being insoluble in excess of the precipitant, may be easily separated from intermixed oxide of lead. This salt dissolves readily in nitric acid; it becomes black in the light; it is decomposed at a red-heat, yielding a residue of metallic silver and protoxide of lead, and is reduced by hydrogen to a gentle temperature, forming an easily fusible alloy of the two metals.[2]

PROTOXIDE OF LEAD HEATED WITH VARIOUS METALLIC OXIDES.—Protoxide of lead forms fusible compounds with various metallic oxides, of which many are infusible *per se;* and this is one of its most valuable properties in relation to metallurgy. Upon this property, together with its highly oxidizing power—or, what is equivalent, the facility with which it is reduced—depends the application of lead in the refining of silver and in the assaying of the alloys and ores of that metal, and of other argentiferous matters.

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[7] Bonsdorff, Répertoire de Chimie, 1838, 3. p. 44.

[8] Liebig u. Kopp, Jahresb. 1855, p. 296. Quoted from Comp. Rend. 41. p. 509.

[9] Ibid.

[1] Handwörterbuch der reinen u. angewandten Chemie, 1842, i. p. 825.

[2] Handwörterbuch, i. p. 825.

It is important to know the fusibility of mixtures of protoxide of lead with the following metallic oxides. The proportion of litharge is given for the fusion of 1 part by weight of each oxide.

Dioxide of copper. Cu^2O.—Litharge 1·5 part. Ratio[3] of Cu^2O : PbO. The molten product is very liquid, and passes through clay crucibles with great facility. There can be no doubt that much less litharge than the proportion above stated would suffice for the fusion of dioxide of copper, but how much less has not been ascertained by experiment.

Protoxide of copper. CuO.—Litharge 1·8 part. Ratio[4] of CuO : PbO. The molten product does not, like the last, run through clay crucibles. The smallest proportion of litharge needful for the fusion of 1 part of protoxide of copper has not, so far as I am aware, been determined.

Oxide of zinc. ZnO.—Litharge 8 parts.[5] With 7 parts the product is pasty.

Iron-scales.[6]—This mixture of protoxide and sesquioxide of iron melts very easily with 4 parts of litharge. Berthier describes the product as compact, opaque, with an even and bright fracture, somewhat metallic in lustre, and very strongly magnetic.[7] The same authority states that spathic iron ores, even the magnesian varieties, melt very well with 4 parts of litharge. The products are brown-black, opaque, even in fracture, and highly magnetic: the colour of their powder is dirty bottle-green. A little of the litharge is always reduced in the process, with, doubtless, the peroxidation of an equivalent proportion of protoxide of iron.

Sesquioxide of iron. Fe^2O^3.—It melts promptly with 10 parts of litharge. According to Berthier the product is compact, with an even and somewhat bright fracture, opaque, and liver-coloured, staining the crucibles fine porphyry-red. When sesquioxide of iron is melted with 20 parts of litharge, and the mass is suddenly cooled, the product is described as compact, vitreous, and brilliant on fracture; and the light transmitted by thin pieces of it is fine hyacinth-red. But if the molten product be left to cool slowly, it separates into two layers, the lower one consisting of pure litharge, and the upper one apparently identical with that obtained, as above stated, by fusing sesquioxide of iron with 10 times its weight of litharge.[8]

Protoxide of manganese. MnO.—With 10 parts of litharge the product was found by Berthier to be very liquid, and to crystallize in large plates like litharge of a clear olive-green colour. With 4 parts of litharge the product melted, but was pasty: it was bubbly, partly crystalline and partly compact, opaque, and dark greenish-grey. No lead was reduced with either of these proportions of litharge.[9]

Stannic acid. Peroxide of tin. SnO^2.—With from 12 to 13 parts of litharge, according to Berthier, there is complete liquefaction; and the product is compact, opaque, dirty-yellow, and with a scaly fracture. With 6 parts of litharge the mass is only softened by heat, not melted.[1]

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[3] Metallurgy, First Part, p. 253.
[4] Ibid. p. 253.
[5] Ibid. p. 539. Berthier, Tr. des Essais, 1. p. 515.
[6] See Metallurgy, Iron and Steel, p. 21.
[7] Tr. des Essais, 1. p. 513.
[8] Ibid. 1. p. 513.
[9] Ibid.
[1] Ibid. p. 515.

Titanic acid. TiO^2.—It requires not less than 8 parts of litharge. The product is compact, opaque, pale coffee-brown, with an even and shining fracture.[2]

Oxide of antimony. SbO^3.—It melts with litharge in all proportions.[3]

Antimonious acid. SbO^4. SbO^3+SbO^5.—For a good fusion Berthier recommends not less than 5 parts of litharge.[4]

Arsenious acid. AsO^3.—A mixture of this acid and litharge in certain proportions melts easily. The following experiments were made by Mr. Smith:—

I.— PbO : AsO^3.
II.—4PbO : AsO^3.

In No. I. the quantities taken were of arsenious acid 495 grains, and protoxide of lead 560 grains. The product melted readily at dull redness, and when cold was an opaque orange-yellow glass.

In No. II. the quantities taken were of arsenious acid 99 grains, and protoxide of lead 448; the mixture readily fused. The product was compact, apparently quite homogeneous, glassy, or wax-like, opaque, and of an agreeable delicate orange-yellow colour. A button of lead was found, which weighed only 28 grains, a proportion so small that it may be practically disregarded. Hence, it may be concluded that arsenious acid is not in sensible degree converted into arsenic acid by fusion with litharge; for in that case lead would be separated in considerable quantity, unless we admit what seems extremely improbable under these conditions, namely, the formation of suboxide of lead.

Berthier made similar experiments, with an additional one in the ratio 2PbO : AsO^3.

Arsenic acid. AsO^5.—Berthier heated mixtures in the following ratios:—

I.— PbO : AsO^5.
II.—2PbO : AsO^5.
III.—4PbO : AsO^5.

The products were as liquid as water while molten, and compact when solid. No. I. was transparent, with a slightly conchoidal and somewhat crystalline fracture. No. II. was slightly translucent, enamel-white, a little blueish from the presence of copper, granular and lamellar in fracture. No. III. was pale-yellow and dull, uneven in fracture, shining, presenting at the surface and in cavities crystals in long, delicate, slightly translucent prisms.[5]

OXIDIZING ACTION OF LITHARGE.—In the metallurgy of silver litharge plays an important part as an agent of oxidation. The most noteworthy results of this action are as follow:—

Sulphur.—Litharge in excess heated with sulphur converts it wholly into sulphurous acid, with the reduction of an equivalent proportion of lead. No sulphate of lead is formed.[6]

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[2] Berthier, Tr. des Essais, 1. p. 513. [3] Ibid. p. 515. [4] Ibid.
[5] Ibid. p. 516. [6] Ibid. p. 382.

Selenium.—Berthier states that when litharge is heated with selenium, not the slightest trace of lead is reduced. Litharge and selenium melt together, and combine, he says, in all proportions, forming products exactly resembling those which result from the fusion of mixtures of selenide of lead and litharge. When these products contain more than 10% of selenium, their colour is black more or less intense, and their appearance is metalloidal: with a less proportion their colour is grey or olive; and 1% of selenium suffices to communicate to litharge a decided olive tint. The whole of the oxide of lead may be dissolved out by hydrochloric acid, the selenium being left pure, or mixed with a little silica from the crucible. Sulphur may be completely separated from selenium by fusion with litharge.[7]

Tellurium.—This metal is converted into telluric acid when heated with litharge, which, if in excess, retains in combination the whole of the telluric acid. But if the litharge be not in excess, most of the telluric acid is volatilized, and telluride of lead is produced.[8]

Arsenic.—If metallic arsenic be heated with litharge in the ratio of As: 4PbO, it appears, from Berthier's experiments, to be wholly converted into arsenious acid (AsO^3) with the separation of 3 equivalents of malleable lead; and the formation of a slag, dark olive-grey, very crystalline, and largely lamellar. There was no fume during fusion.

In the ratio of As: 2PbO, the product consisted of a button of metal semi-ductile, in fracture like galena, but less blue, and of glassy transparent slag of the finest orange-yellow colour.

In the ratio of As: PbO, the product consisted of a button of metal largely lamellar, and of compact, glassy slag of a fine orange-yellow colour. There was much arsenical fume during fusion.[9]

Conversely, metallic lead with the aid of heat partially reduces arsenious acid. Berthier melted 12·40 grammes of arsenious acid with 38·80 of lead shavings, *i.e.* nearly in the ratio of $AsO^3 : Pb^3$. The product consisted of 32 grammes of arsenide of lead, semi-ductile, granular in fracture, very dark grey, and of glassy arsenite of lead having the finest orange-yellow colour.[10]

Antimony.—The two following experiments were made by Berthier. A mixture of 10 grammes of antimony in powder and of 40 of litharge, yielded by fusion a button of lead weighing 23 grammes, and a well-melted compact slag of a fine topaz-yellow colour.

A mixture of 10 grammes of antimony in powder and 80 of litharge, yielded by fusion a button of lead weighing 26 grammes, and a very liquid glass, which after rapid cooling was opaque and resembled yellow wax.

Berthier observes that the antimony was oxidized only to the minimum (SbO^3), otherwise much more lead would have been separated.[1]

The next experiment was made by Smith. A mixture of antimony in powder and litharge in the ratio of Sb: 4PbO was heated to

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[7] Berthier, Tr. des Essais, 2. p. 680. [8] Ibid. 1. p. 382. [9] Ibid. p. 383.
[10] Ibid. [1] Ibid.

redness in a covered clay crucible and melted readily. The quantities taken were 194 grains of antimony and 672 of litharge. The product consisted of a button of impure lead weighing 374 grains, and of a slag, glassy and amber-coloured. The button was hard, cracked at the edges under the hammer, and was easily broken across.

Tin.—The three following experiments were made by Berthier. Tin-foil cut up into very small pieces was mixed with litharge and heated. A mixture of 10 grammes of tin and 37·5 of litharge, yielded an unfused scoriform mass, dull grey, and containing shots of lead [or alloy?] at the bottom. Berthier remarks that if the tin had been oxidized to the *maximum*, all the litharge would have been reduced; and he therefore infers that only protoxide of tin had been formed, which remained in combination with the unreduced litharge.

A mixture of 10 grammes of tin and 80 of litharge, yielded a metallic button weighing 26 grammes, and a slag, pasty while molten, compact, opaque, dull, and greyish-yellow.

A mixture of 10 grammes of tin and 120 of litharge, yielded a metallic button weighing 26·3 grammes, and a very liquid slag, compact, opaque, granular in fracture, and greyish-yellow.[2]

If only protoxide of tin had been formed in the last two experiments, not more than 17·5 grammes of lead should have been separated, so that admitting no other agent for the reduction of the litharge than tin to have been present, it is clear that some peroxide of tin must have been produced, unless we admit what is not probable, namely, that some of the litharge may, in the presence of protoxide of tin, have passed to a higher degree of oxidation.

The next experiment was made by Smith. A mixture of finely-divided tin (obtained by shaking the molten metal during solidification, and afterwards sifting) and litharge in the ratio of Sn : 3PbO was heated to strong redness in a covered clay crucible during ¾ hour. The quantities taken were 148 grains of tin and 840 of litharge. The product was an imperfectly fused mass, with a button of metal at the bottom not well separated.

Bismuth—Berthier has recorded only the following experiment. A mixture of 20 grammes of bismuth and 40 of litharge, yielded on fusion a button of metal weighing 24·3 grammes, ductile and tin-white, and a crystalline slag similar in appearance to pure litharge. As no analysis of the button was made, the proportion of bismuth oxidized cannot be inferred with certainty; but Berthier remarks, that if it had been wholly converted into oxide, the button would have been pure lead and have weighed 28·5 grammes. He concluded that about half of the bismuth had been oxidized, and suggests that this result might be due either to the great fusibility of the metal, whereby it partially escaped from the action of the litharge, or, as he conceives to be more probable, to the fact that protoxide of lead saturated with oxide of bismuth loses the power of oxidizing the latter metal.[3]

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[2] Berthier, Tr. des Essais, 1. p. 383.

[3] Ibid. p. 384.

Copper.[4]—When heated with litharge it is converted into dioxide, but not in the least degree into protoxide, an equivalent proportion of lead being separated. The resulting dioxide of copper combines with or dissolves in the excess of litharge. In an experiment in which copper was heated with 21 times its weight of litharge, not less than $\frac{1}{6}$ of the metal remained unoxidized.

Zinc.—In an experiment by Berthier in which 10 grammes of zinc-filings were heated with 100 of litharge, reaction took place as soon as the latter began to soften; there was ebullition with a slight flame of zinc. On raising the temperature the mass perfectly liquefied: the product consisted of a button of pure lead weighing 13 grammes, and slag, crystalline like litharge, but in very small plates, opaque, and pale yellow. One fifth of the zinc had been volatilized, and the slag should have been composed of 87·7% of oxide of lead and 12·3% of oxide of zinc.[5]

The following experiment was made by Smith. Zinc finely divided by trituration while hot, was mixed with litharge in the ratio of Zn : 2PbO, and exposed in a covered clay crucible to a red-heat during 1½ hour. The quantities taken were 160 grains of zinc and 1120 of litharge. The product consisted of a button of malleable lead weighing 245 grains, and of slag, the central part of which seemed not to have been melted, while the rest or outer part was compact, vitreous or resin-like, dark brown, and impregnated with shots of metal. This outer part of the slag had probably obtained silica derived from the crucible.

Iron.—The two following experiments were made by Berthier. 10 grammes of iron-wire cut up were heated with 100 of litharge, and the mass became pasty but not liquid. The product consisted of a button of lead weighing 40 grammes, and slag, which was compact, opaque, dark metalloidal black, very magnetic, and resembling a forge-cinder (basic silicate of protoxide of iron); a few shots of lead were observed in it, but it was free from metallic iron: it should have consisted of 55·9% of oxide of lead and 13·4% of oxide of iron.

10 grammes of iron-wire were heated with 160 of litharge. The mass became very liquid. The product consisted of a button of lead weighing 46·6 grammes, and slag which was compact, opaque, with uneven fracture, shining, very dark brown and somewhat metalloidal, and highly magnetic. If in these experiments, remarks Berthier, only protoxide of iron had been formed, 38·85 grammes of lead should have been separated; but if magnetic oxide had been formed, 51·8 grammes of lead should have been separated. It was considered probable that an intermediate oxide identical with *iron-scale* had been produced.[6]

The following experiment was made by Smith. Iron in filings was heated in a covered clay crucible with litharge in the ratio of Fe : 2PbO. The quantities taken were 140 grains of iron and 1120 of litharge. Fusion was effected at a bright red-heat. The product con-

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[4] See Metallurgy, First Part, p. 250.
[5] Tr. des Essais, 1. p. 384. See Metallurgy, First Part, p. 539.
[6] Tr. des Essais, 1. p. 385.

sisted of a button of lead weighing 530 grains, containing only a trace of iron, and of slag, which was compact, semi-vitreous, with an even fracture, dark brownish-black, magnetic, and contained shots of lead. The button and slag could not be easily separated from each other. No metallic iron was perceived. The total quantity of lead in the litharge used is 1040 grains, so that a little more than half of the latter had been reduced.

Hydrated Protoxide of Lead.

$2PbO+HO$.—It is a white powder, which loses its water at a temperature somewhat above 100° C. and turns red litmus-paper blue. It readily absorbs carbonic acid, so that in contact with the air it cannot be preserved without change. It is thrown down by the addition of potash to a solution of acetate of lead, but the precipitate contains some subsalt of lead, which may be dissolved out by digestion with a slight excess of the alkali, a little of the hydrate being also dissolved.[7] Schaffner states that when the hydrate is thus prepared from a solution of nitrate of lead, it is intermixed with subnitrate, which cannot be separated by long digestion with an excess of alkali, even though the temperature at last be raised to 90° C.[8] This chemist has confirmed the accuracy of the formula given above; but according to Winkelblech pure hydrated protoxide cannot be obtained by either of the processes above described.[9] Hydrated protoxide of lead is produced by the joint action of air and pure water upon chemically pure as well as impure lead, and in the entire absence of carbonic acid. The formation also under these conditions of crystallized anhydrous protoxide of lead has been previously recorded.

Payen has described a hydrate of protoxide of the formula $3PbO+HO$, which he prepared as follows:—120 parts by measure of a saturated solution of tribasic acetate of lead were mixed with 60 of water previously boiled during half an hour. On the other hand, 4 parts by measure of ammonia-water were diluted with 60 of water also deprived of gas and cooled to 30° C. These two solutions being at the temperature of 25° C. were mixed together in a vessel immersed in a water-bath at 30° C., stirred for an instant, and then left at rest. The mixed solution remained transparent during the whole period of the reaction, which became manifest in about an hour. Crystals continued to be deposited during many hours afterwards. They were in the form of brilliant transparent scales of a yellowish silvery tint, with a slight greenish reflection and were metallic in lustre. They were remarkable especially on account of their refractive power, which caused them to sparkle with all the colours of the spectrum. Under a simple microscope they were found to be regular octahedrons.[1] Ber-

[7] Berzelius, Traité de Chimie, 2. p. 582.
[8] Handwörterbuch, Supplementband, 1850, p. 566. Quoted from Ann. der Chemie, 51. p. 175.
[9] Berzelius, Jahresb. 17. p. 114.
[1] Ann. de Chim. et de Phys. 1837, 66, p. 54.

zelius considered the existence of this hydrate to be doubtful.[2] When hydrated protoxide of lead is boiled with a dilute solution of potash, it is transformed into crystals of anhydrous protoxide.[3]

Sesquioxide of lead.

Pb^2O^3.—It is described by Winkelblec has a fine, amorphous, red-yellow powder. With concentrated hydrochloric acid it forms a soluble yellow chloride, which immediately afterwards is resolved into chloride of lead and free chlorine. Oxalic and formic acids are decomposed by it with the evolution of carbonic acid; and by the action of sulphuric, nitric, or acetic acid a salt of protoxide of lead is produced, peroxide of lead being (PbO^2) separated.[4] Winkelblech prepared it as follows: the precipitate from the addition of caustic potash to a solution of acetate of lead (*sugar of lead*) was well washed and dissolved in a solution of caustic potash; and this solution was mixed with cold hypochlorite of soda free from lime, when after a while began to fall a yellow oxide which gradually turned reddish. This precipitate is the sesquioxide and requires only to be washed and dried, but it obstinately retains hygroscopic water. S. Hausmann has confirmed Winkelblech's results; but he found that the precipitate after desiccation between 140° C. and 150° C. retained 1·2% of water, and that it absorbed carbonic acid from the atmosphere without change of colour.[5]

Caustic alkalies and their carbonates decompose the solution of the sesquioxide of lead, forming a precipitate of the colour of hydrated sesquioxide of iron. This precipitate may be washed with boiling water and dried at 100° C. without either losing its water or changing its colour; and heated to 150° C. it becomes dark coloured like ignited sesquioxide of iron, yet without decomposing. If a fixed alkali is used it cannot be completely washed out of the precipitate, which readily dissolves in a slight excess of the alkali. The sesquioxide of lead may be obtained pure by pouring its solution in acetic acid into greatly diluted caustic ammonia, quickly removing the precipitate thereby formed from the liquor, and washing it with hot water to which a very little acetic acid has been added in order to separate any carbonate which may be present. The sesquioxide thus made differs much in appearance from that prepared by Winkelblech's process, although it agrees with the latter in composition and in chemical reactions.

Jacquelain found that a mixture of protoxide and peroxide of lead, corresponding to the formula $PbO+PbO^2$, heated to 450° C. in a closed glass tube became red, and that some oxygen was disengaged. The product dissolved in glacial acetic acid without any residue of peroxide of lead; and alkaline lye was unable to extract protoxide of lead from it in quantity worth mention.

On similarly heating a mixture, corresponding to the formula $2PbO+PbO^2$, less oxygen was evolved, and the product which like-

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[2] Traité, 2. p. 583.
[3] Fremy, Ann. de Chim. et de Phys. 1844, 12. p. 489.
[4] Berzelius, Jahresb. 17. p. 115.
[5] Liebig u. Kopp, Jahresb. 1854, p. 361.

wise acquired a fine red colour, dissolved completely in alkaline lye and glacial acetic acid.[6]

Red-lead. Minium.

Pb^3O^4.—It is regarded as a salt of the formula $2PbO+PbO^2$, but sometimes it is represented by the formula $PbO+Pb^2O^3$. It occurs in the state of amorphous powder. Karsten states its specific gravity to be 8·62 and Boullay 9·19.[7] It is almost a nonconductor of electricity.[8] It has a fine bright red or orange-red colour, the tint varying with the mode of preparation. When heated it becomes darker in colour, and at a temperature near, yet sensibly below, redness, it is dark purplish-brown or almost black; but its original colour returns as it cools. At a strong red-heat it is resolved into protoxide of lead and oxygen. It is insoluble in water. Nitric acid converts it without the aid of heat into nitrate of the protoxide which dissolves, and peroxide which is left as a puce-coloured powder. Heated with sulphuric acid, 3 equivalents of sulphate of protoxide of lead are formed and 1 of oxygen is set free. Similarly, by the action of hydrochloric acid it is changed into 3 equivalents of chloride of lead with the evolution of 1 of chlorine; but with less acid than suffices for this reaction, chloride and peroxide of lead are produced. It dissolves in cold strong acetic acid, forming a colourless solution, which either when heated or diluted with water lets fall peroxide of lead. The process of manufacturing red-lead will be given in the sequel.

Peroxide of Lead. Puce-Coloured Oxide. Plumbic Acid.

PbO^2.—It has a dark chocolate brown or puce colour, and is usually in the state of amorphous powder, but it also occurs in crystals. The mineral, Plattnerite, is peroxide of lead crystallized in hexagonal prisms belonging to the rhombohedral system: it is stated to have been found at Leadhills in Scotland, but the locality is considered doubtful. According to Becquérel, when peroxide of lead is kept for some time in molten potash, and the mass after cooling is washed with water so as to remove all that is soluble, the residue consists of protoxide and peroxide of lead, each in crystals.[1] In three determinations of the specific gravity of peroxide of lead the extremes are 8·903 and 9·190.[2] It is insoluble in water. At a red-heat it is resolved into oxygen and protoxide of lead: and at a lower temperature into oxygen and red-lead. By the action of solar light it is also reduced to red-lead with the evolution of oxygen. It is a strong oxidizing agent. It incandesces in sulphurous acid at ordinary temperatures, sulphate of protoxide of lead being the product; it also incandesces when triturated with $\frac{1}{6}$th of its weight of cane-sugar, or $\frac{1}{6}$th of grape-sugar. By

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[6] Handwörterb. der rein. u. angewand. Chem., Supplementband, 1850, p. 567. In the Compt. Rend. 31. p. 626, there is only a very short notice of Jacquelain's observations on this subject.

[7] Handwörterbuch, 1. p. 826.

[8] Ibid.

[1] Traité d'Électricité, 1855, 2. p. 129.

[2] Gmelin, Handbook, 5. p. 121.

trituration with $\frac{1}{6}$th of its weight of sulphur, the latter is ignited and burns with a bright flame, sulphide of lead being the product. A mixture of 2 parts of peroxide of lead and 1 of sulphur ignites when touched with sulphuric acid; and if the mixture also contains phosphorus it explodes violently on trituration.[3] It is instantly reduced to protoxide by oxalic acid, which has no action on red-lead. Nitrate of dioxide of mercury, as well as sulphurous acid, also reduces it to protoxide, though neither acts upon red-lead.[4]

Peroxide of lead has been clearly proved by Fremy to act the part of an acid, and he accordingly designates it *plumbic acid* and its salts *plumbates*. Plumbate of potash may be made by boiling for some time in a silver crucible a mixture of peroxide of lead and potash with a small quantity of water. The peroxide disappears and combines with the alkali. If the product be treated with a little water and the solution slowly evaporated, fine, transparent, white rhomboidal crystals of plumbate of potash are deposited. This salt cannot be obtained by heating peroxide of lead with a dilute solution of the alkali, because it is stable only in a strongly alkaline solution. It is very deliquescent; it dissolves without decomposition in an alkaline solution, but with pure water it forms a brown liquor, which contains biplumbate of potash, and from which hydrated plumbic acid is afterwards precipitated. At a high temperature it is decomposed with the loss of its water, oxygen being afterwards disengaged. Its formula is $KO,PbO^2 + 3HO$. Plumbate of soda may also be prepared by the process above described; but it is less soluble in water than plumbate of potash, and when acted upon by water it becomes yellow and soon afterwards brown. Insoluble plumbates may be easily made by heating with access of air a mixture of protoxide of lead and the base. Thus plumbates of lime and baryta may be prepared by calcining mixtures of litharge and these bases, when the peroxidation of the protoxide of lead takes place very rapidly. By the addition of an alkaline plumbate to a solution of litharge in potash-lye, a copious yellow precipitate of hydrated minium is immediately produced, which on slight desiccation is changed into anhydrous minium of a very fine red colour. Hydrated minium becomes also dehydrated in a strong solution of potash. All oxides soluble in potash may be converted into insoluble plumbates by means of plumbate of potash.[5]

From the following observations of Jacquelain peroxide of lead would seem to have basic properties. When a large quantity of red-lead is dissolved in glacial or crystallizable acetic acid at 40° C., yet not enough to saturate all the acid, on cooling acetate of peroxide of lead is deposited in isolated four-sided prismatic crystals. But if too much red-lead is added, water is displaced to such an extent from the hydrate of the acid by the metallic base, which enters into combination, as so greatly to dilute the remaining acid that the salt decomposes and brown

[3] Gmelin, Handbook, 5. p. 122.
[4] Levol, Ann. de Chim. et de Phys. 1840, 75. p. 111.
[5] Ann. de Chim. et de Phys. 1844, 12. p. 490.

peroxide of lead is precipitated. However, the solution of peroxide of lead in glacial acetic acid is not decomposed by dilution with from 4 to 6 times its volume of alcohol of sp. gr. 0·8287. The salt dissolves in a mixture of alcohol and æther. The crystals may be dried somewhat between blotting paper; but on renewing the paper in order to dry them completely, they become yellow and are resolved into acetic acid and dark-coloured peroxide of lead: while still moist with acetic acid they may be kept unchanged in closed glass vessels. They melt at 160° C., and at a somewhat higher temperature they are quickly and completely decomposed, yielding a residue of metallic lead and a Tonka bean-like odour of acetone with some acetic acid. Water resolves them into their components, peroxide of lead and acetic acid; whereas a solution of sesquioxide of lead in acetic acid is resolved by water into peroxide and acetate of protoxide of lead.[6]

Peroxide of lead may be conveniently prepared by digesting red-lead with pure and somewhat dilute nitric acid until everything soluble is completely removed. Nitrate of protoxide of lead is formed and dissolves, while peroxide of lead is left as an insoluble powder, which must be thoroughly washed and carefully dried. The digestion may be aided by heat even to boiling; but Levol asserts that when red-lead is treated with nitric acid of the sp. gr. 1·152, and heat applied, some of the resulting peroxide of lead is decomposed, and a little of it even dissolves, colouring the liquor violet.[7] Peroxide of lead is produced by the action of chlorine water upon red-lead, or by heating the aqueous solutions of certain lead-salts, *e.g.* the acetate, with hypochlorite of soda.[8]

As the peroxide is largely consumed in the manufacture of lucifer-matches, much attention has of late been directed to its preparation, and many practical details on the subject have been published. Böttger recommends the following process:—Finely-sifted acetate of lead (*sugar of lead*) is boiled vigorously in a capacious porcelain basin with an excess of a filtered and clear solution of hypochlorite of lime, the mixture being well stirred; and the boiling is continued until the odour of chlorine is replaced by that of acetic acid. The whole of the lead in the acetate should be converted into peroxide; and when this is the case, sulphuretted hydrogen-water added to a little of the filtered liquor causes no browning. If the action is completed, the supernatant liquor should be decanted and the peroxide of lead washed with distilled water upon a filter until the wash-water, on being tested with oxalate of ammonia, is found to be free from lime. The peroxide is described as dark-brown, and of a granular crystalline appearance. It would be difficult, it is affirmed, to produce equally pure peroxide of lead at a less cost by any other method. According to the same chemist, all the lead of freshly precipitated chloride may be easily converted into peroxide by boiling with a solution of hypochlorite of

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[6] Handwörterbuch der rein. u. angewandt. Chem. Supplementband, 1850, p. 566.

[7] Ann. de Chim. et de Phys. 1840, 75. p. 111.

[8] Gmelin's Handbook, 5. 121.

lime.[9] Puscher states that white-lead, litharge, or red-lead may be converted into peroxide of lead by boiling with a clear solution of hypochlorite of lime.[10] In Wöhler's process a solution containing 4 parts by weight of crystallized acetate of lead is mixed with a solution containing 3 parts, or better somewhat more, of crystallized carbonate of soda. Carbonate of lead is precipitated, whereby a thin pasty mass is formed, and into this chlorine gas is to be passed until the whole of the carbonate of lead is converted into the dark-brown peroxide, which must be thoroughly washed, and which amounts to 2½ parts. Chloride of sodium is produced, but no chloride of lead, acetic and carbonic acids being set free.[11] Overbeck advises the preparation of peroxide of lead by boiling hydrated protoxide of lead with ferridcyanide of potassium (*red prussiate of potash*) and potash.[12] Levol says that protoxide of lead, obtained by the calcination of white-lead, may be converted into peroxide by gently heating 100 parts of it in admixture with 25 of chlorate of potash and 200 of nitre; but the temperature must not reach even *dull redness*, as in that case red-lead would be produced. The heating must cease as soon as the mass has acquired a dark and uniform black tint, which with the proportions above prescribed generally happens when the whole is completely molten. It is easy so to peroxidize $\frac{9}{10}$ths of the protoxide of lead, and after having well washed this product, the unchanged remaining $\frac{1}{10}$th may be dissolved out by digestion with nitric acid. The peroxide thus made is nearly black. Levol states that red-lead cannot, like protoxide of lead, be converted into the peroxide by heating it with chlorate of potash.[13]

LEAD AND SILICON.

Berzelius states that lead and silicon combine when heated together before the blowpipe, forming a malleable product, which by the solvent action of acids yields an insoluble residue of silica.[1] This is a subject which requires further investigation.

Silicates of Protoxide of Lead.

These silicates, and their reactions of metallurgical interest, have been carefully examined in my laboratory by Dr. Beck, of Darmstadt, and upon his results the following description is, for the most part, founded. Silica and protoxide of lead easily combine, even when only heated to the degree at which the oxide becomes pasty. In preparing these silicates by the *dry* way, it is not expedient at once to raise the temperature so high as perfectly to melt the oxide, for, in that case, the silica would mostly rise to the top of the liquid oxide, and might remain there a considerable time uncombined. At the beginning, the temperature should merely suffice to render the

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[9] Wagner's Repertorium, 1858, p. 232; 1859, p. 248.

[10] Liebig u. Kopp, Jahresb. 1856, p. 395.

[11] Ibid. 1854, p. 362.

[12] Ibid. 1856, p. 395.

[13] Ann. de Chim. et de Phys. 1840, 75. p. 109.

[1] Gmelin's Handbook, 5. 165.

oxide pasty, so that the silica and oxide may be kept as largely in contact as possible, in order to promote combination, after which it should be raised high enough to melt the silicate formed. Moreover, by this mode of proceeding, which is commonly known as fritting, the corrosive action of the molten oxide upon the substance of the earthen crucible which may be used in the process is lessened to the utmost. Platinum vessels, indeed, might be employed, provided no agent capable of reducing the oxide has access; and it was of such vessels that Faraday availed himself in his investigation concerning the borosilicate of lead proposed to be applied to optical purposes, on account of its great refractive power. The materials from which silicates of lead may be conveniently made are fine white sand and red-lead, such as are adapted for the manufacture of flint glass, which is composed of silica, protoxide of lead, and potash. Red-lead, when heated with silica, loses part of its oxygen, and is reduced to protoxide. Silicates of lead may also be made by adding an aqueous solution of soluble alkaline silicate, like the silicate of soda or water-glass, to aqueous solutions of salts of lead, say, the nitrate. All the fusible silicates of lead are yellow, of which the tint deepens in proportion to the quantity of protoxide of lead present; and unless special precautions are taken in their preparation to avoid the presence of oxide of iron, they are apt to be more or less brown. All silicates of lead in which the silica does not exceed the proportion in the formula $PbO,2SiO^3$ are vitreous, and transparent after fusion. They refract light powerfully and have a bright lustre, and both these properties increase in proportion to the quantity of oxide of lead. The fusibility of the silicates of lead varies directly in a greater or less degree with the quantity of oxide of lead which they contain. Thus the silicate prepared according to the formula $3PbO,SiO^3$, may, while melted, be poured out almost like water, while that prepared according to the formula $2PbO,SiO^3$, can scarcely be poured out at all. Mixtures of oxide of lead and silica made according to the formulæ $PbO,3SiO^3$ and $PbO,4SiO^3$, could not be melted, but formed a white, uniform, porcelain-like mass; and the products of mixtures containing yet more silica were white and porous, consisting seemingly of uncombined silica and silicates of lead richer in oxide sintered together.

Dr. Beck experimented upon intimate mixtures of red-lead and fine siliceous sand in the proportions indicated by the formulæ in the following table, in which are also stated the actual quantities employed, and the percentage composition of the products. The heating was effected in Cornish crucibles, with the precautions previously notified as to temperature, and the exclusion of reducing agents. It is essential in the preparation of silicates of lead by the dry way to prevent access of the reducing gases of the furnace to the interior of the crucible; and this condition may be secured by placing the crucible *on the top* of the fuel, and leaving the mouth of the furnace more or less open. It is not to be supposed that in every instance the product was a definite silicate; and indeed it is certain that some

of the products were only mixtures of a definite silicate with uncombined base, or with uncombined acid. Further, it was not clearly demonstrated which products were definite silicates, owing to the fact that the protoxide of lead and silicates of lead are both fusible, and may be melted together in all proportions with the formation of products, which, after solidification, appear homogeneous. Many experiments were made to ascertain whether by cautiously pouring out the molten contents of the crucible under varying conditions as to temperature of melting and rapidity of cooling, separation or liquation of products, differing in degree of fusibility, would occur, as is the case with the products obtained by melting certain mixtures of oxide of iron and silica, and the results were either inconclusive or absolutely negative.

The colour of the silicates of lead may be completely changed by the presence of the oxides of some other metals. A small quantity of sesquioxide of iron suffices to render them brown. Thus on re-melting the silicate, prepared according to the formula $3PbO,SiO^3$ from a mixture of 2100 grains of red-lead and 280 grains of silica, with only 30 grains of iron-filings, there was produced a dark-brown, almost black, glass, scarcely transparent at the edges. When silicate prepared according to the formula $3PbO,2SiO^3$ was melted with a trace of sulphate of copper or blue vitriol, the product was a beautiful green glass; and these green silicates became yellow when melted with lead. The colours, especially yellow, appear much darker while the silicate is hot. Silicates which are green when cold sometimes appear yellow while hot. When silicate prepared according to the formula PbO,SiO^3 was melted with a trace of Swedish pyrolusite (black oxide of manganese, MnO^2), it became dark-red, almost black, and scarcely transparent at the edges.

	Quantity operated upon in grains.		Composition of product per cent.	
	Red-lead.	Silica.	Protoxide of lead.	Silica.
I. $3PbO,SiO^3$	2320	300	88·1	11·9
II. $2PbO,SiO^3$	2320	450	82·6	17·4
III. $3PbO,2SiO^3$	2320	600	79·2	20·8
IV. PbO,SiO^3	2320	900	71·1	28·9
V. $2PbO,3SiO^3$	2320	1350	62·2	37·8
VI. $PbO,2SiO^3$	700	580	55·2	44·8
VII. $PbO,3SiO^3$	·470	550	45·1	54·9
VIII. $PbO,4SiO^3$	400	620	38·1	61·9
IX. $PbO,12SiO^3$	350	1740	13·9	83·1

Nos. I., II., III., IV., melted easily at comparatively low temperatures, and the products were perfectly vitreous. No. V. required a rather high temperature for its fusion, but the product was also perfectly vitreous. No. VI., at a high temperature, fritted into a compact, white, opaque, porcelain-like mass, which, on being re-melted at a higher temperature, became a perfect glass. No. VII. could not be melted into glass, but formed a compact, homogeneous, porcelain-like

mass. No. VIII. yielded a white, compact mass, with only a few cavities in it. No. IX. fritted into a white, porous mass.

According to Berthier, No. III. suffices for all assays in which a silicate of lead may be required, and this silicate is stated to be "preferable to litharge in assaying substances free from silica, but containing earths or oxides which alone do not combine with oxide of lead, except through the intervention of silica. In order to liquefy these substances, at least as much silicate of lead must be employed as would be required of litharge; but with the silicate is obtained a homogeneous combination, in which no metallic particles can remain in suspension, while with litharge, as the earths are only mixed, there is not the same certainty of accurately separating from it the metallic particles which it may be necessary to extract."[2]

Nos. I., II., III., dissolved easily and completely in boiling dilute nitric acid. No. I. was not wholly decomposed by, or soluble in, acetic acid. No. IV. was not completely decomposed by nitric acid, even after evaporating three times to dryness. No. I. dissolves completely in a warm, aqueous solution of caustic potash, while the silicates richer in silica dissolve but imperfectly in such a solution, and less in proportion to the quantity of silica which they contain.

The vitreous silicates of lead do not blacken in air like that of a chemical laboratory, which may contain a small quantity of sulphuretted hydrogen, whilst the enamel-like and spongy-white silicates quickly blacken in such an atmosphere; but the vitreous as well as the other silicates immediately become black in pure sulphuretted hydrogen gas.

Silicates of protoxide of lead heated with sulphur.—The following experiments were made by Dr. Beck:—I. 1000 grains of silicate prepared according to the formula $3PbO,SiO^3$ were heated with 350 grains of sulphur. Effervescence occurred, and when this had entirely ceased, 500 grains of lead were put into the crucible, with a view to collect any lead or sulphuretted lead which might have been separated. The product consisted of a button weighing 748 grains, which was very malleable, though apparently not quite free from sulphur; and of transparent yellow glass, just like the original silicate. Supposing the lead reduced to be pure, the composition of the glass would be represented by the formula $2PbO,SiO^3$.

II. 750 grains of silicate prepared according to the formula PbO,SiO^3 were heated with 250 grains of sulphur. The product consisted of a homogeneous, black, obsidian-like glass, which contained only 0·075% of sulphur; and of a few metallic globules at the bottom, seemingly of sulphuretted lead, which weighed only 10 grains. From these experiments it appears that some sulphide of lead is produced, according to the formula $2PbO+S^3=2PbS+SO^2$, and that reaction follows between the sulphide and oxide of lead, as will be hereafter

[2] Tr. des. Ess. 1. p. 517.

explained, whereby lead is set free, and sulphurous acid evolved. The reducing action of sulphur on silicates of lead is very limited.

Silicate of lead heated with protosulphide of iron.—The two following experiments were made by Dr. Beck:—

I. The mixture was composed of 1420 grains of silicate prepared according to the formula $3PbO,SiO^3$, and 100 grains of protosulphide of iron, FeS, so that the ratio of the oxide of lead in the silicate to the sulphide of iron was 125 : 10. The product consisted of a black glass, which contained 0·12% of sulphur; and of a crystalline, fine-grained, somewhat malleable metallic button, which weighed 325 grains.

II. The mixture was composed of 1710 grains of the same silicate as used in the preceding experiment and 50 grains of protosulphide of iron, so that the ratio of the oxide of lead in the silicate to the sulphide of iron was 300 : 10. The product consisted of a black glass, which appeared brown at the thinnest edges, and a button, apparently of pure lead, which weighed 145 grains.

The conclusion from these experiments is, that in respect of oxidizing effect this silicate of lead resembles litharge. (See Appendix.)

Silicates of protoxide of lead heated with wood charcoal.—Many experiments have been made in my laboratory by Dr. Beck, in order to ascertain the action of charcoal as a reducing agent upon silicates of lead prepared according to various formulæ, and the results are of sufficient interest and practical importance to be recorded in detail.

Silicate made according to the formula PbO,SiO^3 was intimately mixed with excess of charcoal-powder (*i.e.* considerably more than sufficient to reduce the whole of the oxide of lead in the silicate), and strongly heated in a covered Cornish crucible. The product was not a coherent mass, and no button of lead was formed. The charcoal was separated by washing with water, and the residue consisted of hollow globules, varying in size from less than a pin's-head to a small pea. The substance of which these singular bodies were composed was white, grey, or light yellowish-brown, opaque, and more or less vitreous or enamel-like within, as seen on fracture. They were studded both on their external and internal surfaces with minute firmly-adherent shots of lead. Some of these globules contained transparent glass, which was probably silicate of lead in its original state. When the silicate of lead was heated with only just sufficient charcoal to reduce the whole of the protoxide of lead, a coherent grey mass of hollow globules, with a small quantity of interposed charcoal, was obtained.

A mixture of 1000 grains of the same silicate and 50 grains of charcoal-powder was heated as above described, and the product, after washing off the residual charcoal as completely as possible with water, was melted with carbonate of soda. By this means the contents of the crucible were perfectly fused; and, when cold, consisted of a single button of lead, covered with a layer of transparent green glass. In two similar experiments of this kind the buttons of lead weighed 385 and 365 grains; and as the quantity of silicate of lead

operated upon (1000 grains) contained 770 grains of lead, the loss was 385 and 405 grains respectively. But no confidence should be placed in these numbers, as the experiments were only tentative; and, indeed, under any circumstances, it would be impossible to prevent very notable loss of lead in such experiments. When the same mixture of silicate and charcoal was not so strongly heated as in the foregoing experiments, no hollow globules were formed, and only 245 grains of lead were obtained by subsequent fusion with carbonate of soda.

In experimenting in the same way upon other very fusible silicates prepared according to the formulæ $3PbO,SiO^3$—$2PbO,SiO^3$—$3PbO,2SiO^3$, it was found necessary to heat the mixtures very gradually, for otherwise part of the silicate subsided unchanged in a molten state to the bottom of the crucible. But by properly regulating the temperature, hollow globules were formed without either the separation of a button of lead, or of unchanged silicate. The globules were larger than those produced from the silicate composed according to the formula PbO,SiO^3; they were also more coherent, and had more lead adherent to their external surface. Some of these globules were observed to consist of three layers; an outer and an inner layer of opaque white enamel-like substance, and an intermediate layer of transparent glass, which was probably undecomposed silicate. When these more fusible silicates were mixed with sufficient charcoal for the complete reduction of their oxide of lead, a small button of lead was found at the bottom of the crucible under a layer of glass, probably of unchanged silicate, and above this glass was a mass of hollow globules and intermixed charcoal-powder. The product obtained by heating a mixture of 1000 grains of silicate prepared according to the formula $3PbO,SiO^3$ with 50 grains of charcoal, yielded, after washing with water, and fusion with carbonate of soda, as previously described, a button of lead which weighed 405 grains. In another similar experiment with 60 instead of 50 grains of charcoal, the button of lead weighed 469 grains. Supposing, what is certainly not true, namely, that these numbers represent the total quantity of lead reduced, the substance of the globules would have been composed of silicate approximating to the formula $PbO,2SiO^3$. In three similar experiments with mixtures of 1000 grains of silicate, made according to the formula $2PbO,SiO^3$, and of 50 grains of charcoal, buttons of lead were obtained which weighed respectively 640, 580, and 570 grains. The weights of the last two buttons would lead to the inference that a silicate of the formula $PbO,2SiO^3$ had been left unreduced. Two other similar experiments were made with a mixture of 440 grains of the silicate represented by the formula PbO,SiO^3 and of 40 grains of charcoal, and with a mixture of 700 grains of the silicate represented by the formula $PbO,3SiO^3$, and of 30 grains of charcoal; the buttons of lead weighed respectively 255 and 80 grains, thus showing how imperfect was the reduction. As lead was separated from the last-named highly acid silicate, it seems probable that this silicate was only a mixture of one containing more base with free silica.

The conclusion from the preceding experiments is, that when any compound of silica and protoxide of lead is strongly heated in intimate mixture with more charcoal than would suffice for the complete reduction to the metallic state of the whole of the oxide of lead if uncombined, a considerable portion of the oxide remains unreduced. After reduction has proceeded to a certain extent, a comparatively infusible substance, consisting either of a very acid infusible silicate or of a mixture of free silica and fusible silicate, is produced, which is not acted upon by charcoal, even at a white-heat. The formation of the hollow globules, caused doubtless by the liberation of the gaseous products of reduction under special conditions, must obviously tend to check reduction, by preventing contact between the reducing agent and their internal surface. In order completely to reduce protoxide of lead in combination with silica by solid carbonaceous matter, it is essential to add a flux, which will form a fusible compound with silica.

Silicate of protoxide of lead heated with carbonate of soda and charcoal, and with carbonate of lime and charcoal.—Dr. Beck obtained the following results :—

I.—The mixture was composed of 500 grains of silicate, of the formula PbO,SiO^3, 600 grains of carbonate of soda, and 35 grains of charcoal. These proportions more than suffice to form tribasic silicate of soda, $3NaO,SiO^3$. The product consisted of a transparent green glass, and a button weighing 330 grains. There is probably an error here, as the total weight of the lead present was only 330 grains, and some loss must have occurred.

II.—The mixture was composed of 500 grains of the same silicate, 320 grains of carbonate of lime, and 35 of charcoal. The proportions suffice to form bibasic silicate of lime, $3CaO,2SiO^3$. A higher temperature was needed for fusion than in the last experiment. The product consisted of a well-melted green glass, which had a tendency to become stone-like, and a metallic button which weighed 210 grains. The total quantity of lead in the silicate operated upon was 330 grains, so that either much loss must have occurred, or reduction have been incomplete, and the latter inference is probably correct; the slag was a well-melted glass. Now bibasic silicate of lime is with difficulty fusible, *per se*, but would become easily fusible by the addition of oxide of lead. The substance of the crucible may, however, have acted as a flux.

Silicates of protoxide of lead heated with iron.—At a bright red-heat the lead of all the fusible products obtained by heating oxide of lead and silica together, is completely separated in the metallic state by iron, with the formation of silicate of protoxide of iron, resembling tap-cinder of the puddling-furnace. The proportion of iron employed should be at least equal to what would be required to produce silicate of the formula $3FeO,SiO^3$. Thus, $3PbO,SiO^3 + Fe^3 = 3FeO,SiO^3 + Pb^3$. With such highly siliceous and imperfectly fusible products as No. IX. of the Table p. 29, the separation of the lead by iron must necessarily be incomplete, because iron can only exert its reducing action when

in direct contact with the subject of reduction; and in the case in question contact must obviously be partial, unless, indeed, the iron were in the state of fine powder and intimately mixed with the material operated upon. The following results, obtained in my laboratory, are given in illustration :—

I.—1000 grains of silicate, prepared according to the formula $3PbO,SiO^3$, and containing, therefore, 81·6% of lead, heated with 400 grains of iron, gave a button of lead which weighed 790 grains, and a highly crystalline, opaque, dark-coloured slag. The total quantity of lead in the silicate was 816 grains. (Dr. Beck.)

II.—700 grains of silicate, prepared according to the formula $3PbO,2SiO^3$, and containing, therefore, 72·8% of lead, heated with 200 grains of iron, gave a button of lead which weighed 470 grains. The total quantity of lead in the silicate was 509 grains. (Dr. Beck.)

III.—This experiment was made by Smith. Silicate of lead, prepared according to the formula $2PbO,SiO^3$, and containing 77·24% of lead, gave by fusion in an iron crucible 73·73% of lead. On re-melting the resulting slag of silicate of protoxide of iron in the same crucible, 0·55% of additional lead was separated, and the slag retained 0·30% of lead. The loss of lead by volatilization amounted to 2·66%. The details of this experiment will be found in the Appendix.

Silicates of protoxide of lead heated with sesquioxide of iron and charcoal.—The following experiments were made by Dr. Beck. The mixtures operated upon were as under :—

	Weight of silicate in grains.	Weight of oxide of iron in grains.	Weight of charcoal in grains.
I. $3PbO,SiO^3$	500	400	65
II. $2PbO,SiO^3$	1000	500	130
III. PbO,SiO^3	500	400	60

No. I.—The product consisted of a highly crystalline, opaque, dark-brown slag, and a homogeneous, soft, malleable, metallic button, a little harder than lead, which weighed 495 grains, and contained iron mechanically diffused. Its specific gravity was 9·50. The slag was free from lead, and contained 37·76% of silica, which indicates for its formula $2FeO,SiO^3$. It presented large planes on cleavage.

No. II.—The reaction did not appear to have been complete. A metallic button was obtained, which weighed 980 grains. It was neither so soft nor so malleable as the button in No. I. It contained iron mechanically intermixed, of which the particles could be felt by cutting with a knife. It evolved hydrogen in sensible quantity, when acted upon by hot hydrochloric acid.

No. III.—The product consisted of brown, stone-like slag, and a metallic button which weighed 230 grains.

The conclusion is, that by the addition of a mixture of oxide of iron and charcoal, in suitable proportions, to silicates of lead—

namely, sufficient charcoal to reduce the sesquioxide of iron to protoxide, and the whole of the oxide of lead in the silicate to the metallic state, and sufficient protoxide of iron to form a bibasic silicate of iron—the lead is as completely separated as when metallic iron is directly used, though a higher temperature and a longer time are required. The reduction of the lead may in this case be due to metallic iron reduced from the sesquioxide of iron by charcoal; and that some iron was reduced is clear from the foregoing data. In any case protoxide of iron may be regarded as virtually the agent whereby complete reduction of the lead is effected, as it liquefies the silica; and unless this occurred the whole of the lead could not be set free. Supposing iron to be reduced in the first instance, it is afterwards converted into oxide, in exerting its reducing action on oxide of lead.

Silicates of protoxide of lead and potash.—Common flint-glass is a compound silicate of this nature. It possesses great lustre and high refractive power, which increases with the proportion of lead. Accordingly, it is used by opticians in achromatic lenses, and for that purpose must contain more oxide of lead than common flint-glass, and be absolutely free from striæ. But the besetting evil of such glass is striæ, which are due to want of homogeneity, as though the glass were only an imperfect mixture of two silicates differing in specific gravity. The evil was first surmounted by Guignand; and, thanks to the labours of M. Bontemps, it is now an article of regular manufacture. Thorough mixture of the molten contents of the glass-pot, and slow cooling, so as to keep the temperature of the pot as uniform as possible in every part, are the conditions to be attained as far as practicable.

In 1840, the late Mr. G. Dollond, favoured me with the following tabulated statement of the composition of various specimens of heavy optical glass, as determined by Mr. Faraday, dated September 2nd, 1824:—

	I a. Green colour.	I b. Tint inclining to green.	II. Tint inclining to brown.	III. Tint inclining to green.	IV. Colourless.	V. Tint inclining to pink.
Specific gravity	3·453	3·4387	3·283	3·2715	3·2904	3·616
Silica.....	49·16	48·24	51·93	52·31	51·66	44·30
Protoxide of lead.....	39·66	40·12	33·28	33·06	36·16	43·05
Potash	10·70	10·60	13·77	13·79	11·47	11·75
Oxide of iron	0·10	0·08	0·13	0·17	0·11	0·12
Alumina	0·25	0·58	0·47	0·41	0·43	0·50
Oxide of manganese	..	..	0·14	..	trace	slight trace
	99·87	99·62	99·72	99·74	99·83	99·72

I*a*.—Holmes' heavy or achromatic flint-glass.

I*b*.—Ditto do. do. do. not so heavy as No. I*a*.

II.—Holmes' usual or common flint-glass.

III.—Green's flint-glass for optical purposes.

IV.—Part of a 46-inch object-glass from "the famous pot" of flint-glass.

V.—Guignand's flint-glass.

Silicates of protoxide of lead and soda.—Dr. Beck heated mixtures of litharge, carbonate of soda, and quartz sand, in the proportions indicated by the following formulæ :—

I.—$PbO,2NaO + 6SiO^3$.
II.—$PbO, NaO + 4SiO^3$.

No. I. gave a well-melted, transparent, nearly colourless glass ; and No. II. a well-melted, transparent light-green glass.

Silicate of protoxide of lead and baryta.—By strongly heating, in a covered clay crucible, a mixture consisting of 23 parts by weight of red-lead, 17·5 of nitrate of baryta, and 21·5 of silica, I obtained a well-melted, transparent, heavy-green glass, which should approximate in composition to Guignand's heavy flint-glass, with the substitution of baryta for potash in that formula.

Silicates of protoxide of lead and lime.—Berthier heated mixtures of litharge, carbonate of lime, and quartz sand, in the proportions indicated by the following formulæ :—

I.—$3CaO, 3PbO + 2SiO^3$.
II.—$3CaO, 6PbO + 2SiO^3$.
III.—$3CaO, 9PbO + 2SiO^3$.
IV.—$3CaO,12PbO + 2SiO^3$.

No. I. was not softened. No. II. was much softened, without melting. No. III. became pasty. No. IV. perfectly melted, and the product was compact, granular, slightly crystalline, opaque, and of the yellow colour of protoxide of lead. If caustic lime is used instead of carbonate, the mixture need not be so strongly heated, and fusion readily takes place, and much more readily still if combination between the lime and silica has been effected before the litharge is added.[3]

Dr. Beck heated mixtures of red-lead, carbonate of lime, and quartz sand, in proportions indicated by the following formulæ :—

I.—$PbO,CaO + 2SiO^3$.
II.—$PbO,CaO + 4SiO^3$.

No. I. gave a transparent light-green glass, a little less fusible than silicate of lead made according to the formula PbO,SiO^3. No. II. was not melted, but only fritted into a white porous mass.

Silicate of protoxide of lead, lime, and alumina.—Berthier found that a mixture of 5 parts by weight of litharge, 1 of chalk, and 1 of clay (the kind of clay is not specified), melted pretty easily, and when cold the product was compact, opaque, greyish, and had a waxy fracture.[4]

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[3] Tr. des Ess. 1. p. 511.

[4] Ibid. p. 512.

LEAD AND SULPHUR.

Sulphide of Lead.

PbS.—It is the chief ore of lead known as galena. It may be directly and easily formed by heating a mixture of sulphur and lead, when combination occurs below redness and is attended with incandescence. The temperature should be raised to bright redness, in order thoroughly to melt the product, which is very brittle, blueish-grey, and on fracture bright, metallic, and crystalline, and in all respects like that of native sulphide. After fusion sulphide of lead does not decrepitate when heated. When sulphuretted hydrogen is passed into an aqueous solution of a salt of lead, sulphide of lead is thrown down as a black amorphous powder, which, by fusion, acquires the same characters as the sulphide above described. It crystallizes in the cubical system. The specific gravity of the finest natural galena is 7·585. It melts at a strong red-heat into a thin liquid, which rapidly filters through the usual kinds of earthen crucibles, without corroding their substance. While molten it volatilizes sensibly, and in a degree proportionate to temperature; and its vapour, if protected from oxidation, condenses in a crystalline form. A simple and pretty experiment is to put some galena at the bottom of a plumbago crucible, then fill up with fragments of charcoal, lute on a cover, heat strongly, and leave the crucible to cool gradually in the furnace. Beautiful crystals of sulphide of lead will be found deposited on the charcoal. Care, however, must be taken not to heat too high or too long, in which case no sulphide may remain.

Sulphide of lead, beautifully crystallized, not seldom occurs as a sublimate in certain metallurgical processes. Its volatilization is promoted by currents of gas, such, for example, as proceed from the combustion of fuel. According to Collet-Descostils, sulphide of lead in volatilizing is resolved into supersulphide which escapes, and into subsulphide which remains;[5] but this statement is not justified even by his own experiments on the subject; and it is opposed to the fact, that the sulphide of lead, occurring as a sublimed furnace product, is ordinary sulphide, and not supersulphide.[6] Moreover, Rammelsberg ascertained that the composition of sulphide of lead is not changed by fusion.[7] Berthier found that sulphide of lead, exposed during an hour in a covered brasqued crucible to 50° of Wedgwood's pyrometer, lost 40% of its weight, and to 150° not less than 75%.[8]

When molten galena is poured into cold water, the odour of sulphuretted hydrogen is evolved, the granulated product is remarkably friable, and a sensible quantity of black powder is found, which, for the most part, floats on the surface of the water. Galena also, by being merely heated to low redness, and then plunged into cold water, becomes excessively friable, hardly, if at all, less so than when granulated.

By the action of somewhat dilute cold nitric acid, sulphide

[5] Journ. des Mines, 27. p. 466. 1810.
[6] E. Metzger, Hütten-Erzeugnisse, p. 351.
[7] Lehrb. der chem. Metallurgie, 2nd ed. p. 221.
[8] Tr. des Essais, 2. p. 670.

of lead is decomposed, with the formation of nitrate of protoxide of lead, the evolution of nitric oxide gas, and the separation of sulphur. Strong fuming nitric acid oxidizes both elements of the sulphide, and converts it into sulphate, with the liberation of nitric oxide. Hydrochloric acid changes it into chloride of lead, with the evolution of sulphuretted hydrogen; and the white pigment known as Pattinson's oxychloride of lead, is prepared from a solution of chloride of lead, obtained by digesting galena in hydrochloric acid. When sulphide of lead is heated in chlorine, chloride of lead and chloride of sulphur are produced.

Sulphide of lead heated with other metallic sulphides.—True chemical compounds seem to be formed when sulphide of lead is heated with various metallic sulphides; but their formulæ for the most part have not been satisfactorily determined, nor, indeed, have their physical characters been carefully examined and described. The published information respecting these compounds is loose, meagre, and, in some cases, erroneous.

Double sulphides of lead and sodium or potassium are dark-grey and easily fusible. They are decomposed and quickly disintegrated by water, which dissolves out alkaline sulphide free from lead, leaving sulphide of lead in the state of very fine black powder.

Some double sulphides of iron and lead are described in the second volume of this work, entitled 'Metallurgy of Iron and Steel.'

The following experiments on heating sulphide of lead and sulphide of antimony in various proportions have been made in my laboratory by my former student J. C. Cloud. Mixtures of the two sulphides were melted together under charcoal in covered luted crucibles for about 10 minutes, and afterwards allowed to cool slowly.

I. $6PbS+SbS^3$, the formula of Kilbrickenite.
II. $5PbS+SbS^3$, the formula of Geocronite.
III. $3PbS+SbS^3$, the formula of Boulangerite.
IV. $2PbS+SbS^3$, the formula of Jamesonite.
V. $PbS+SbS^3$, the formula of Zinckenite.
VI. $4PbS+3SbS^3$, the formula of Plagionite.

The results are as follow:—

I. The product was homogeneous and brittle; the fracture was crystalline, metallic in lustre, and blueish-grey.

II. The product was brittle and crystalline throughout, but not homogeneous; the fracture at the upper part was granular-crystalline, and at the lower part more largely crystalline; the lustre was metallic, and the colour less blue at the upper part.

III. The product resembled No. II.

IV. The product was brittle and homogeneous; the fracture was finely granular-crystalline, metallic in lustre, and blueish-grey.

V. The product was homogeneous and brittle; the fracture was silky, metallic in lustre, and blueish-grey.

VI. The product was homogeneous and brittle; the fracture was acicular crystalline, metallic in lustre, and blueish-grey.

Supposed Subsulphides of Lead.

It has been generally admitted that definite subsulphides may be formed by melting sulphide of lead and metallic lead mixed in equivalent proportions, care being taken to prevent oxidation from access of atmospheric air. Thus, subsulphides of the formulæ Pb^5S and Pb^4S have been described. It is true that in this manner apparently homogeneous and definite compounds may be obtained. A mixture, for example, in the ratio PbS : Pb yields a product harder than lead, somewhat malleable, crystalline on fracture, dark-grey, more fusible and less lustrous than galena. Sulphide of lead and lead may be melted together in all proportions, and in external characters the products approximate to sulphide of lead or lead, according as one or the other predominates. If, after fusion, cooling be rapidly effected, the mass may seem to be homogeneous throughout; but if, on the contrary, cooling take place slowly, the mass will be found to consist of soft, malleable, and comparatively pure lead at the bottom, and of hard crystalline sulphide of lead at the top. No distinct line of separation will be visible, and the passage from soft lead to hard sulphide is more or less gradual. We have made careful and repeated experiments on this subject, and the results are confirmatory of the foregoing statement. The following experiment was made in my laboratory, conjointly by my former assistant Mr. Dick, and by Mr. Smith. Lead of the best quality and galena yielding by assay 81% of lead, were the materials employed.

The weight of lead was 30,840 grains.
Ditto galena 2347 „

The galena and part of the lead were heated under charcoal in a Cornish crucible, until the mass became soft, when the remainder of the lead was added and the temperature raised sufficiently to cause perfect fusion. After well stirring the molten metal with a charred stick, the crucible was taken out of the furnace. The charcoal covering the metal was removed, after which, as cooling occurred, a little oxide of lead was at first formed on the surface. This oxide was scraped off, and then sulphuretted lead was observed rising to the surface in spots, and of this a portion (a) was collected by skimming. The stirring and skimming were continued until sulphuretted metal ceased to come up, and then the residual lead was cast in the form of an ingot (b). The sulphuretted metal, except the portion first taken off, was pressed between hot bricks, when liquid lead flowed out and sulphuretted lead was left (c).

Supposing no loss to have occurred in melting together the lead and galena, the product should have contained 7·07% of galena or 0·945% of sulphur.

The sulphuretted metal (a) contained 1·14% of sulphur, which is equivalent to 8·57% of sulphide of lead (PbS).

The lead (b) contained only 0·013% of sulphur, which is equivalent to 0·098% of sulphide of lead.

The liquated residue (c) contained 1·906 of sulphur, which is equivalent to 14·288% of sulphide of lead.

Experiments of this kind made, on a small scale, in crucibles, are apt to lead to erroneous conclusions, as it is difficult to recognize the effect of liquation in a little button of metal. Yet even Fournet, whose authority is cited in support of the existence of definite subsulphides of lead, observed that the button obtained by melting together galena and metallic lead in the proportion of 15 parts by weight to 39 "appeared a little more ductile at the bottom than at the top,"[9] lead free from sulphide having, in a certain degree, subsided.

Before describing the reactions of special metallurgical interest connected with sulphide of lead, it will be convenient to treat of sulphate of lead, a knowledge of which, as will presently be perceived, is essential to the understanding of some of those reactions.

ULPHATE OF PROTOXIDE OF LEAD.

PbO,SO^3.—It is anhydrous. It is thrown down as a white amorphous powder, when dilute sulphuric acid or an aqueous solution of a soluble sulphate, say sulphate of soda, is added to an aqueous solution of a salt of lead, such as the nitrate or acetate. It is formed, though slowly, by the action of concentrated boiling sulphuric acid on lead, and it is the product of the feebly corrosive action of cold sulphuric acid upon lead, with access of atmospheric air. Sulphuric acid combines directly with protoxide of lead, and, with the aid of heat, it converts the higher oxides of lead into sulphate of the protoxide, with the evolution of oxygen. This sulphate occurs beautifully crystallized in the prismatic system in Nature, in some cases seemingly as the result of atmospheric oxidation of galena. Sulphate of lead dissolves in hot hydrochloric acid, and as the solution cools, brilliant colourless crystals of chloride of lead are deposited. The sulphuric acid in sulphate of lead may be accurately determined by pouring a hot solution of this salt in hydrochloric acid into a dilute solution of chloride of barium in water, when the whole of the sulphuric acid will be thrown down in combination with baryta. It is slightly soluble in hot, strong, but not dilute, nitric acid; in certain saline solutions, especially in that of acetate of ammonia; in strong sulphuric acid, from which it is precipitated on the addition of water; and it is least soluble in dilute sulphuric acid and acetic acid.

It is converted into carbonate of protoxide of lead, even at the ordinary temperature, by the solutions of fixed alkaline carbonates, neutral as well as acid, of carbonate of ammonia,[10] and, it may be added, of bicarbonate of lime, and by boiling in water with carbonate of lime. It is not absolutely insoluble in water, 1 part, according to Fresenius, dissolving in 22,186 parts of pure water at 11° C., and in 36,504 of dilute sulphuric acid.[1] Sulphate of lead

[9] Ann. des Mines, 3 s. 4. p. 229.
[10] Traité complet de Chimie Analytique. H. Rose, 1. p. 132.
[1] Gmelin, Handbook, 5. p. 138.

is permanent at a low red-heat, but care must be taken to prevent access of reducing agents. Berthier states, that at a strong white-heat it softens and becomes enamel-like, with the evolution of a little sulphurous acid.[2] Heated to bright redness in an earthen crucible, sulphuric acid is evolved, and the residue is a pale-yellow, crystalline, basic sulphate; the silica in the substance of the crucible doubtless interfering in a certain degree, and forming silicate of lead. The yellow basic sulphate of lead obtained by melting the neutral sulphate in a Cornish crucible has been analysed by Smith and found to be composed as follows:—

Protoxide of lead	80·78
Alumina, Sesquioxide of iron	0·72
Sulphuric acid	15·78
Silica	2·72
	100·00

It dissolved in hydrochloric acid without residue, thus shewing that the whole of the silicate was present in a state of combination. Now, in order to form silicate of lead, according to the formula PbO,SiO^3, 6·62 of protoxide of lead are required; and in order to form the silicate, according to the formula $3PbO,SiO^3$, 19·86 of the protoxide are required. Taking the first formula as the most probable, the 100 parts of the basic sulphate of lead in question might be represented as composed of about 89·94 parts of sulphate of lead of the formula $3PbO,SO^3$, and 9·34 of silicate of lead of the formula PbO,SiO^3.

The following experiments have been made in my laboratory by Smith. The sulphate of lead operated upon was prepared by the addition of sulphuric acid to nitrate of lead; and the sulphate was heated in a platinum dish, and, except in the first two experiments, in a muffle.

(1). 100 grains were subjected, over an air-gas burner, to a low red-heat, and suffered no loss in weight.

(2). 100 grains of the sulphate which had been operated upon in the preceding experiment were heated strongly over the blowpipe air-gas burner (*i.e.* with a jet of air from double bellows in the centre of the flame), when a trace of fume was evident: the loss in weight amounted to 0·07%.

(3). 100 grains were heated in a muffle at a red-heat during more than half an hour, but there was no appearance of softening. At a strong red-heat, however, softening occurred, and not until 10 minutes after the first sign of it was observed did complete fusion take place: no fume was perceived while the sulphate remained in the muffle; but on withdrawing the platinum dish, slight fume became visible. The loss in weight amounted to 8·57%. The product was white, pearly in lustre, and somewhat crystalline.

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[2] Tr. des Ess. 2. p. 676.

(4). 100 grains heated to low whiteness during 10 minutes became rapidly very liquid, with the evolution of copious dense fumes. The loss in weight amounted to 19·54%. The product was crystalline and pale greyish-yellow.

(5). 20 grains subjected to a white-heat during about three-quarters of an hour were wholly volatilized: at first dense white fumes were evolved, which towards the end became more dense and dark-grey. The platinum was not acted upon. The products Nos. 3 and 4 were analysed, and found to be composed as under: in the first column the percentage composition of sulphate of lead is given for the sake of comparison:—

	Sulphate of lead.	Product No. 3.	Product No. 4.
Protoxide of lead	73·62	79·86	86·93
Sulphuric acid	26·38	20·14	13·07
	100·00	100·00	100·00

In No. (3) Of 100 grains of sulphate	Remained	91·43	composed of	Protoxide of lead	73·02
				Sulphuric acid ...	18·41
	Volatilized	8.57	,,	Protoxide of lead	0·60
				Sulphuric acid ...	7·97
					100·00

In No. (4) Of 100 grains of sulphate	Remained	80·46	composed of	Protoxide of lead	69·94
				Sulphuric acid ...	10·52
	Volatilized	19·54	,,	Protoxide of lead	3·74
				Sulphuric acid ...	15·80
					100·00

The fixed product in No. (3) may be represented by the formula $7PbO+5SO^3$
or, $4(PbO,SO^3)+3PbO,SO^3$
The fixed product in No. (4) may be represented by the formula $7PbO+3SO^3$
or, $PbO,SO^3+2(3PbO,SO^3)$.

Action of hyposulphite of soda on sulphate of lead.—In the Jahresbericht for 1858, p. 186, it is stated that an aqueous solution of hyposulphite of soda dissolves sulphate of lead, owing to the formation of a double salt. On leaving the solution exposed to the air, sulphide of lead is produced in small quantity; but on boiling, this sulphide is precipitated in large quantity. By the addition of acids, sulphate of lead and free sulphur are formed. The accuracy of this statement has been confirmed by Mr. J. C. Cloud, in my laboratory.

Sulphate of lead heated with fixed alkaline carbonates, or with lime.—Sulphate of protoxide of lead is decomposed at a red-heat by carbonate of soda or potash, or by lime, with the formation of alkaline sulphate, or sulphate of lime and protoxide of lead.

Sulphate of lead heated with silica and certain silicates.—It is decomposed at a red-heat by silica, with the formation of silicate of protoxide of lead, and the escape of sulphuric acid, which may be partially resolved into sulphurous acid and oxygen. However, the preparation of silicates of lead in this manner from the sulphate requires a longer time and a higher temperature than by the heating of mixtures of prot-

oxide of lead and silica. The combined silica of certain silicates, such as clay, which is silicate of alumina, acts like free silica upon sulphate of protoxide of lead, and hence this salt, Berthier suggests, might be used instead of galena, or other compounds of lead, in the glazing of pottery, or even instead of minium in the manufacture of flint-glass;[3] but it is doubtful whether that suggestion would succeed in practice.

Sulphate of lead heated with borax.—A mixture, in the proportion of one equivalent of each, *i.e.* 60% of sulphate and 40% of borax, gave a fusible, transparent, yellow, vitreous product. If earthen crucibles are used in this experiment, the odour of sulphurous acid is perceived, and is caused by the action of the silica in the substance of the crucible upon the sulphate of lead, the sulphuric acid being partially resolved into sulphurous acid and oxygen.[4]

Sulphate of lead heated with protoxide of lead.—Sulphate of lead is easily fusible in admixture with protoxide of lead; and according to Berthier, 10% of litharge suffices to render the sulphate as liquid as water at a white-heat. A mixture of the sulphate and oxide in the ratio of PbO : PbO,SO^3 melts readily at dull redness into a pale yellow crystalline product, similar to that obtained by heating to bright redness the sulphate *per se*, and no fumes of sulphuric acid are disengaged. A definite basic sulphate of lead appears to be thus formed.

Sulphate of lead heated with chloride of lead.—A mixture in the ratio PbO,SO^3 : PbCl melted at a red-heat with considerable effervescence, and the evolution of copious opaque fumes; the product, when cold, was a greyish-white compact mass. According to Berthier, only a very small quantity of the chloride is needed to liquefy the sulphate; and with a mixture in the ratio of 4 (PbO,SO^3) : PbCl, *i.e.* containing 18·6% of chloride, the product was perfectly liquid, and, when cold, was a translucent enamel, having an even fracture.[5]

Sulphate of lead heated with alkaline and earthy sulphates.—Mixtures in certain proportions of sulphate of lead and alkaline sulphates melt easily. A mixture of one equivalent of sulphate of soda and one of sulphate of lead, *i.e.* of 32·2% of the former and 67·8% of the latter, was found by Berthier to become as liquid as water at a red-heat and solidified into a compact, opaque mass, having an uneven fracture. Sulphate of lead, on the same authority, does not yield fusible products when mixed with sulphate of baryta, strontia, or lime.[6]

Sulphate of lead heated with chloride of sodium or potassium.—With a mixture in the ratio PbO,SO^3 : NaCl, Berthier obtained a compact, grey, translucent product, having a scaly fracture. Continual ebullition occurred while the matter was molten, and thick vapours of chloride of lead were disengaged.[7] Marguéritte states that when sulphate of lead is heated to redness, either with chloride of sodium or

[3] Berthier, Tr. des Ess. 2. p. 676.
[4] Ibid. 1. p. 480.
[5] Ibid. 2. p. 678.
[6] Ibid. 2. p. 678.
[7] Ibid. 1. p. 500.

potassium, chloride of lead is volatilized and may be condensed, sulphate of the alkaline metal being formed. Chloride of lead in water containing gypsum suspended is changed into sulphate of lead, which may then be heated with alkaline chloride; so that by means of a given quantity of chloride of lead the sulphuric acid of gypsum may be extracted and utilized in the formation of sulphate of soda or potash, and the necessity of manufacturing sulphuric acid for soda-making be rendered unnecessary. So far this seems only to have been a laboratory scheme. According to Nicklès, chloride of sodium is not completely converted into sulphate in the manner above described.[8]

Sulphate of lead heated with fluoride of calcium.—Mixtures in the following ratios were experimented upon by Berthier:—

I.— PbO,SO^3 : CaF = 21%.
II.—$2(PbO,SO^3)$: CaF = 11·6%.
III.—$4(PbO,SO^3)$: CaF = 6·2%.

No. I. melted with the greatest facility, and became as liquid as water. The product was compact, greyish, opaque, with feeble lustre, stony, uneven in fracture, and not in the least degree crystalline. A precisely similar result was obtained in my laboratory by Smith.

No. II. melted as easily and became as liquid as No. I. The product also resembled that of No. I., but was yellowish-white.

No. III. melted when strongly heated, but did not become perfectly liquid. The product was vesicular, the cavities being small; it resembled pumice, was granular, and broke up into grains (*s'egrénant*) under the finger-nail; it was slightly yellowish, and presented no sign of crystallization.[9]

Sulphate of lead heated with fluoride of calcium and lime.—Berthier found that a mixture in the ratio of one equivalent of each, *i.e.* 69% of sulphate of lead, 18·1% of fluoride of calcium, and 12·9% of lime, quickly became very liquid. When cold the product was lamellar and crystalline; the greater part of it was pale-grey and opaque, but towards the bottom it was yellow, which, as Berthier suggests, seems to indicate the separation of oxide of lead, and consequently the formation of sulphate of lime.[10]

Sulphate of lead heated with carbonate of lime, fluoride of calcium, and carbon.—According to Schnederman, when sulphate of lead (air-dried) is heated with 67% of chalk, from 12% to 16% of charcoal, and 37% of fluor-spar, it is completely reduced, the sulphate of lime generated forming an easily fusible mixture with the fluor-spar.[11]

Sulphate of lead heated with sulphate of baryta, sulphate of lime, and fluoride of calcium.—A mixture of these substances in the ratio of one equivalent of each, *i.e.* 40·4% of sulphate of lead, 31·1% of sulphate of baryta, 18·0% of sulphate of lime, and 10·4% of fluoride of calcium,

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[8] Liebig u. Kopp's Jahresb. 1860, p. 693. Compt. Rend. 50. p. 760.
[9] Tr. des Ess. 1. p. 486.
[10] Tr. des Ess. 1. p. 486.
[11] Liebig u. Kopp's Jahresb. 1850, p. 635; and 1852, p. 777.

melted readily, and the product, when cold, was hard, brittle, pale-yellow, having a dull compact fracture, crystalline towards the centre. The experiment was made by Smith in my laboratory.

Sulphate of lead heated with lead.—A mixture in the ratio

$$PbO,SO^3 : Pb$$

yields protoxide of lead as the product, the whole of the sulphur escaping as sulphurous acid, thus:—

$$PbO,SO^3 + Pb = 2PbO + SO^2.$$

The following experiment in illustration was made in my laboratory by Smith:—A mixture of 760 grains of sulphate of lead and 520 grains of finely granulated lead, *i.e.* in the ratio above stated, melted in an earthen crucible, gave a dark amber-coloured vitreous product, and a small button of lead weighing 52 grains. In such experiments it is not possible to obtain an absolutely precise result, owing to the interfering action of the substance of the crucible.

Sulphate of lead heated with cyanide of potassium.—The whole of the lead is reduced to the metallic state, and is usually separated, partly in small globules and partly as black powder, which is quite free from sulphur. A very small quantity of sulphocyanide of potassium is formed. The process is sufficiently accurate for quantitative analysis, and with that object may be conveniently performed in a small porcelain crucible. Commercial cyanide of potassium containing some cyanate of potash may be employed, and in the proportion of about 5 parts by weight to 1 of sulphate of lead.[12]

Sulphate of lead heated with iron.—It is completely reduced with the formation of a considerable quantity of dark-coloured, imperfectly-melted scoriaceous slag. By heating 1000 grains of the sulphate to bright redness in a wrought-iron crucible, with the addition of iron nails, a button of malleable lead was obtained, which weighed 520 grains, the total quantity of lead in the sulphate operated upon being about 680 grains. But under the circumstances, especially the character of the slag, the result, as to degree of reduction, should be only received as roughly approximate.

Special Reactions connected with Sulphide of Lead.

Sulphide of lead heated with protoxide of lead.—When the mixture is such that the sulphur and oxygen are in the same ratio as in sulphurous acid, then, on exposure to a strong red-heat, the whole of the sulphur will be evolved as sulphurous acid, and the whole of the lead reduced to the metallic state.

$$PbS + 2PbO = Pb^3 + SO^2.$$

When in any given mixture of sulphide and oxide of lead the oxygen is in a greater ratio than $O^2 : S$, then the reduced metal will be

[12] Rose, Traité de Chim. Analyt. 2. p. 226.

covered with a layer of protoxide of lead equivalent to such excess. Conversely, when the sulphur is in a greater ratio than S : O^2, then the whole of such excess will be found in the reduced lead rendering it hard and less malleable; or, if the experiment is on a large scale, the sulphide of lead will separate and accumulate at the top.

$$PbS+3PbO = Pb^3+PbO+SO^2.$$
$$2PbS+2PbO = Pb^3+PbS+SO^2.$$

Although it has been practically demonstrated that the foregoing reactions occur, yet it requires much skill in conducting experiments of this kind so as to yield even approximate results. There may be several sources of error, such as the corrosive effect of the materials on the substance of the crucibles, the oxidizing action of the air upon the sulphide of lead, and loss by effervescence caused by the escape of sulphurous acid, as well as by volatilization. The mixture should be as intimate as possible, and the temperature carefully regulated.

Sulphide of lead heated with sulphate of lead.—When the mixture is such that the sulphur and oxygen are in the same ratio as in sulphurous acid, then, on exposure to a strong heat, the whole of the sulphur will be evolved as sulphurous acid, and the whole of the lead reduced to the metallic state.

$$PbS+PbO,SO^2 = Pb^2+2SO^2.$$

When the oxygen is just sufficient to form sulphurous acid and protoxide of lead, then the whole of the sulphur will be evolved as sulphurous acid, and the residue will consist wholly of protoxide of lead; and when insufficient the product will consist of lead and protoxide, thus:—

$$PbS+3PbO,SO^2 = 4PbO+4SO^2.$$
$$PbS+2PbO,SO^2 = Pb+2PbO+3SO^2.$$

Any sulphate of lead exceeding the proportion in the last equation would exist in the residue as yellow basic sulphate. The neutral sulphate at a strong red-heat loses acid and becomes basic; but in the presence of protoxide of lead it combines with the latter, and becomes basic without loss of acid, provided there be enough protoxide, as in the case in question. Conversely, when the proportions are reversed, and the sulphur exists in a greater ratio than S : O^2, the whole of such excess will be found in the reduced lead.

Sulphide of lead heated with access of air.—Sulphurous acid is evolved, and if the process be continued until the odour of that acid ceases to be emitted, and if the temperature be so regulated as never to reach the degree at which protoxide and sulphide of lead decompose each other, the product will consist of protoxide and sulphate of lead. By thus completely roasting 100 parts by weight of pure galena with all possible care, Plattner obtained a bright yellow product, which had increased 3% in weight, and was composed of 66·3 parts of free protoxide of lead, and of 36·7 parts of sulphate of lead.[1] The proportion

[1] Die metallurg. Röstprozesse, p. 145.

of free to combined oxide is nearly as 3 : 1. As galena decrepitates much when heated and is readily fusible, it is necessary in such experiments that it should be in very fine powder, and be very gradually heated.

According to Rodwell sulphide of lead, precipitated from a solution of acetate of lead by sulphuretted hydrogen and dried in a water bath, slowly absorbs oxygen when exposed to the air at 50° C. and upwards. The quantity of oxygen absorbed in a given time increases as the temperature rises. In one experiment the odour of sulphurous acid was evolved at about 150° C., and in another at about 125° C. The sulphide which had thus absorbed oxygen gave off sulphurous acid when gently heated with very dilute hydrochloric, acetic, or tartaric acid, from which it was inferred that *sulphite*, and not sulphate, of lead had been produced. On one occasion sulphide of lead heated to 135° C. became red-hot when blown upon, with the copious evolution of sulphurous acid. It may be added that Rodwell found great difficulty in preparing pure sulphide of lead by precipitation with sulphuretted hydrogen from the solution of a salt of lead, owing to the absorption of oxygen during subsequent desiccation with access of air. He succeeded, however, by passing sulphuretted hydrogen to saturation through water in which the precipitated sulphide was suspended, allowing it to subside, washing and drying at a temperature below 100° C., treating the dry sulphide in a current of dry sulphuretted hydrogen, and finally in pure and dry hydrogen to remove any traces of sulphuretted hydrogen or of sulphur, which it might have contained.[2]

Sulphide of lead heated with access of air in admixture with other sulphides.—Plattner states that by carefully roasting 100 parts by weight of a mixture consisting of 50 parts of galena and 50 of iron-pyrites (FeS^2), there is a loss of 10% in weight, but a relative increase in the proportion of sulphate of lead.[3] He found that such a mixture completely roasted was composed as follows:—

Free oxide of lead	18·3
Sulphate of lead	38·5
Sesquioxide of iron	33·2
	90·0

The proportion of free to combined oxide is nearly as 2 : 3. This increase in sulphate of lead is explained by the fact that during the roasting *sweet* of iron-pyrites, under the usual conditions of a gradually increasing temperature, sulphuric acid is evolved, which, in part, combines with protoxide of lead. For the same reason a similar result may be confidently predicted in the roasting of a mixture of galena and disulphide, or any sulphuretted ore, of copper, or of any other metallic sulphide partially convertible under the circumstances into sulphate, which at a higher temperature is decomposable with the evolution of sulphuric acid.

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[2] Journal of the Chemical Society, New Series, 1863, i. p. 47. [3] Op. cit. p. 145.

Sulphide of lead heated with silicate of lead.—Dr. Beck experimented upon silicates of lead prepared according to five different formulæ in admixture with different proportions of galena. The quantities employed are given in the following table:—

No.	Approximate ratio of silicate to galena.		Weight of silicate operated upon, in grains.	Weight of galena operated upon, in grains.	Ratio between 100 parts of silicate and galena.		Ratio of equivalents of oxygen in the base of the silicate to equivalents of sulphur in galena.	
	Silicate.	Galena.			Silicate.	Galena.	Equivalents of oxygen.	Equivalents of sulphur.
I.	$3(3PbO,SiO^3)$:	4PbS	1,130	500	100	44	9	4
II.	,, :	2PbS	,,	250	,,	22·1	,,	2
III.	,, :	¾PbS	,,	100	,,	8·8	,,	¾
IV.	,, :	½PbS	,,	60	,,	5·3	,,	½
V.	$4\frac{1}{2}(2PbO,SiO^3)$:	4PbS	1,220	500	,,	40	9	4
VI.	,, :	2PbS	,,	250	,,	20·4	,,	2
VII.	,, :	PbS	,,	130	,,	10·6	,,	1
VIII.	,, :	¼PbS	,,	40	,,	8·19	,,	¼
IX.	$3(3PbO,2SiO^3)$:	4PbS	1,260	500	,,	39·6	9	4
X.	,, :	2PbS	,,	250	,,	19·8	,,	2
XI.	,, :	½PbS	,,	60	,,	4·7	,,	½
XII.	$9(PbO,SiO^3)$:	4PbS	1,410	500	,,	35·4	9	4
XIII.	,, :	½PbS	,,	60	,,	4·2	,,	½
XIV.	$14(PbO,3SiO^3)$:	PbS	490	18	,,	37·5	14	1

The results obtained are as follow:—

No. I.—The product consisted of a dark reddish-brown transparent glass and a crystalline, somewhat malleable, metallic button, which weighed 600 grains. This button was not homogeneous: the outer part round the sides was largely crystalline with cubical cleavage; it resembled, but was softer than, galena, and could not be completely reduced to powder without cohering into laminæ; two determinations of the sulphur in it were made, and the results were 7·25% and 7·15%: the principal mass, which could not be distinctly separated from the preceding part, was also crystalline, fine-grained, somewhat malleable, and so soft that it could not be reduced to powder; it contained 1·1% of sulphur: at the bottom there was a thin skin of soft lead.

No. II.—The product consisted of a yellow transparent glass and a metallic button, which weighed 380 grains. This button was homogeneous, crystalline, dull-grey, and not so malleable as pure lead; it contained 0·49% of sulphur.

No. III.—The product consisted of a red-brown transparent glass and a metallic button, perfectly malleable, and nearly as soft as pure lead.

No. IV.—The product consisted of a yellow transparent glass and a button of lead, which weighed about 30 grains.

No. V.—The product consisted of a slag, transparent and light-brown at the top, opaque and dark-coloured at the bottom, and of a homogeneous, metallic, crystalline button, which broke in two under

the hammer; it weighed about 630 grains; it could easily be cut with a knife, and contained 1·89% of sulphur. The dark-coloured part of the slag contained 0·11% of sulphur.

No. VI.—The product consisted of a black slag and a metallic button which weighed 220 grains.

No. VII.—The product consisted of red-brown transparent glass and a metallic button which weighed 90 grains, very malleable, but not so soft as pure lead.

No. VIII.—There was a metallic button which weighed 130 grains.

No. IX.—The product consisted of a transparent, dark red-brown glass and a crystalline, brittle, metallic button, which weighed about 656 grains. It was softer than, but cleavable like, galena, and could not be perfectly reduced to powder; it contained 6·61% of sulphur.

No. X.—There was a metallic button which weighed 280 grains.

No. XI.—There was a button of lead which weighed 35 grains.

No. XII.—The product consisted of opaque, black slag, containing particles of galena, and a button resembling galena, which contained 11·72% of sulphur. A piece of the slag, apparently free from particles of galena, contained 0·49% sulphur, the largest quantity found in any of these slags.

No. XIII.—There was a button of lead which weighed 30 grains.

No. XIV.—The product was a fritted, hard, stone-like, light-grey mass of silicate and intermixed galena, of which small crystals could be distinctly seen.

Various mixtures of the silicates of lead and galena were heated with the addition of a considerable quantity of metallic lead, with the view of more completely collecting the metallic buttons, and the results were similar to those above described. From the preceding data it may be concluded that the silicates of lead are only partially decomposed by galena, and that a very large excess of silicate is needed to cause a separation of comparatively pure lead. It may easily be conceived that as reaction proceeds between the protoxide of lead in the silicate and the galena, the mass becomes less and less fusible, and the conditions consequently less and less favourable to reduction. Besides, a pretty high temperature must be employed in these experiments, in order to produce reaction between the silicate and the sulphide. The black colour of the slags in some of the experiments was due to the presence of sulphide of lead. It was observed that they were always transparent and yellow, if the temperature had been sufficiently high to cause complete reaction; while, on the contrary, if the temperature had been too low, complete separation and subsidence of the sulphide of lead from the slags did not occur, and, in that case, they were always black, and contained a sensible quantity of sulphur. All the metallic buttons produced in the foregoing experiments were crystalline, even when not more than 0·49% of sulphur was present.

Sulphide of lead heated in the vapour of water.—According to Regnault, at dull redness decomposition is hardly perceptible, but at a temperature sufficient somewhat to agglomerate sulphide of lead in

powder yet not to melt it, very feeble action occurs. Sulphuretted hydrogen and protoxide of lead are formed, and the latter decomposes the subjacent sulphide of lead in immediate contact with it, producing sulphurous acid and metallic lead, which will be seen as a pellicle on the residual sulphide, especially after trituration in a mortar. Reaction takes place between the sulphuretted hydrogen and sulphurous acid, with the formation of water and sulphur, which causes milkiness in the water resulting from condensation of the steam employed in the experiment. Some of the sulphide of lead is volatilized in the current of steam and immediately afterwards deposited in small, very bright cubical crystals, and to such an extent in an experiment made by Regnault in a tube of hard green glass, as to line the whole of the tube between the sulphide of lead and the end at which the steam escaped.[4]

Pattinson passed steam during an hour over galena heated to whiteness in an earthen tube. Sulphuretted hydrogen was copiously evolved, and the condensed steam became as white as milk, an effect due not to sulphate of lead as Pattinson inferred, but to the deposition of sulphur caused by contact of the sulphuretted hydrogen with the sulphurous acid resulting from action of the protoxide of lead formed upon the unchanged galena, as previously stated. A cake of fused and partly reduced galena was found in the tube near the end at which the steam entered: it was brittle, yet could be cut with a knife. The tube in the middle contained some brilliant cubical crystals; for the space of three inches near the end where the steam escaped it was nearly filled with beautiful cubes of galena of considerable size; and in the coldest part, near the end projecting from the furnace, there was a deposit of fine blueish-grey powder without cohesion. Not a particle of metallic lead was produced in the operation.[5]

Jordan, of Clausthal, repeated Pattinson's experiment, at a strong red-heat during 3 hours.[6] The gaseous products escaping from the tube were passed into water. Galena in grains of the size of millet seeds was operated upon, and the heating was effected in a glass tube coated externally with clay wrapped round with iron wire. Sulphuretted hydrogen was at first evolved. After some time the water traversed by the escaping gas became milky, and subsequently the odour not of sulphuretted hydrogen, but of sulphurous acid in a slight degree, was perceived; and at this period dark-greyish or brownish-black vapour was emitted from the tube, which rendered scarcely perceptible the milkiness of the water above mentioned. This water now gave an acid reaction with test paper, and was found to contain free sulphuric acid and sulphur, but no sulphate of lead. The dark colour of the vapour was due to sulphide of lead. After the completion of the experiment the tube when cold was broken. It contained a residue of crystallized sulphide of lead, coated with what seemed to be a very thin skin of metallic lead; and here and there above the skin sulphide of lead

[4] Ann. d. Mines, 3 s. 11. p. 47. [5] Phil. Mag. 1829, 5. p. 172.
[6] Erdmann's Journ. 1831, II. p. 348.

was observed in hair-like crystals. The end of the tube which protruded beyond the furnace where the gaseous products escaped was lined with crystals of galena. Neither sulphate nor oxide of lead was perceived in the tube.

At a white-heat sulphuretted hydrogen is copiously evolved by the action of the vapour of water on sulphide of lead, and black powder is condensed along with the steam. This statement is founded on experiments made in my laboratory by Dick. Galena was the material operated upon, and it was introduced into a porcelain tube in a small porcelain boat. In one experiment minute globules of metallic lead were found in the boat. Hair-like crystals were observed in the tube during the course of the experiment on looking in at one end. The results in such experiments will probably vary somewhat with the temperature and the rapidity of the current of steam. The black powder was believed to be sulphide of lead; but whether it was wholly the result of simple volatilization, or might in part proceed from recombination of sublimed lead and sulphur, set free from the action of sulphuretted hydrogen or sulphurous acid, is a question. Sulphurous acid must be formed under the circumstances; for if the hydrogen of the steam combines with the sulphur of the galena, an equivalent proportion of oxygen must unite with the desulphurized lead; but the oxide of lead resulting will instantly act upon the unchanged sulphide of lead in contact with it, and yield sulphurous acid and metallic lead. The following equations will make these reactions clear:—

$$2Pb\,S + 2HO = 2PbO + 2HS.$$
$$2Pb\,O + PbS = Pb^3 + SO^2$$
$$2HS + SO^2 = S^3 + 2HO.$$

It must be borne in mind that in such experiments as the foregoing the presence of a large excess of steam is supposed; for otherwise no such reaction as that last stated could occur, because sulphuretted hydrogen passed over protoxide of lead either cold or heated would cause the production of sulphide of lead and water.

Sulphate of lead heated with carbon.—Gay-Lussac ascertained that when sulphate of lead is heated to dull redness (*rouge-sombre*) with excess of carbon, it is reduced to sulphide with disengagement of carbonic acid quite free from sulphurous acid. If less carbon is added than suffices to form carbonic acid with the oxygen of the sulphate, the product will consist of sulphide of lead, and of sulphate of lead equivalent to the excess of oxygen. On afterwards raising the temperature sufficiently to cause reaction between sulphide and sulphate of lead, namely, to cherry-redness, metallic lead or protoxide of lead will be obtained according to the proportion of carbon employed.[7] The following equations will explain these reactions:—

$$PbO,SO^3 + C^2 = PbS + 2CO^2.$$

[7] Ann. de Chim. et de Phys. 1836, 73. p. 435.

With excess of carbon.

First result at the low temperature:

$$2PbO,SO^3+C^2=PbS+PbO,SO^3+2CO^2.$$

Second result at the higher temperature:

$$PbS+PbO,SO^3=Pb^2+2SO^2.$$

With less carbon.

First result at the low temperature:

$$4PbO,SO^3+C^2=3PbO,SO^3+PbS+2CO^2.$$

Second result at the higher temperature:

$$3PbO,SO^3+PbS=4PbO+4SO^2.$$

This reaction might at first seem out of order in this place; yet it is not, because sulphide of lead which is formed in the process, is mainly concerned in it.

Sulphate of lead heated in hydrogen.—According to the experiments of Rodwell, when sulphate of lead is heated to redness in a current of pure dry hydrogen, water, sulphurous acid, and sulphuretted hydrogen are evolved, with the separation of metallic lead. The quantitative analytical results which he obtained led him to propose the following formula in explanation of the reaction:—

$$2(PbO,SO^3)+H^7=Pb^2+SO^2+HS+6HO.$$ [8]

Sulphate of lead heated in carbonic oxide.—According to Rodwell, sulphurous and carbonic acid are evolved, and lead is reduced. But the results which he obtained in his experiments were not sufficiently conclusive to establish the formula expressing the reaction. He suggests that if it were possible to heat every particle of a mass of sulphate of lead to the same temperature and at the same time in carbonic oxide, it would be decomposed according to the following equation:—

$$2(PbO,SO^3)+6CO=Pb+PbS+SO^2+6CO^2.$$ [9]

Sulphide of lead heated in hydrogen.—According to Collet-Descostils, at cherry-redness, sulphuretted hydrogen is formed, and an equivalent proportion of lead reduced.[1] In a rapid current of the gas some sulphide is volatilized and deposited on reaching a cooler part of the porcelain tube, which was used in the experiment. At low redness I found that sulphuretted hydrogen continued to be evolved in small quantity during several hours.

Sulphide of lead heated in carbonic oxide.—Rodwell found that pure sulphide of lead prepared by precipitation (as described at p. 37) lost, when heated to redness in a porcelain tube in a current of carbonic oxide during half an hour, 0·1623% of sulphur, and when heated to bright whiteness at intervals during the same time, 0·3892%, and 0·4830% in two experiments respectively. The gas on leaving the

[8] Journ. of the Chem. Soc. antea cit. p. 42.

[9] Ibid. p. 44.

[1] Journ. des Mines, 1810, 27. p. 469.

tube was passed into a solution of potash, which became yellow and evolved sulphuretted hydrogen on the addition of a dilute acid, whence he inferred that bisulphide of carbon (CS^2) had been formed.[2]

Sulphide of lead heated with carbonate of soda or potash, or with caustic, soda or potash.—There is only partial reduction of the sulphide and a grey very fusible slag is formed containing sulphate of soda, sulphide of sodium, and sulphide of lead. Berthier found that galena heated in a retort with at least half its weight of carbonate of soda yielded about 53% of lead.[3] The oxygen of the atmospheric air in the retort contributed, as he suggested, to this reduction; and he conjectured that if the experiment were made *in vacuo* only 49% of lead would be reduced. His view of this reaction is expressed in the following formula:—

$$7PbS + 4NaO,CO^2 = NaO,SO^3 + 3NaS + 3PbS + Pb^4 + 4CO^2.$$

It is assumed that the sulphide of sodium produced exists in the slag in combination with sulphide of lead in the proportion of equivalent to equivalent. In the foregoing equation the sulphide of lead and carbonate are in the proportion by weight of 100 : 25, *i.e.* as stated above on the authority of Berthier, only half the quantity of carbonate of soda required to set free 53 parts by weight of lead from 100 of galena when the experiment is not made *in vacuo*.

When atmospheric air has access during the process a much larger quantity, practically even the whole, of the lead may be reduced. At first the reactions shown in the preceding formula occur, and then the further reduction is due to the oxidation of the sulphide of lead in the slag, whereby oxide and sulphate of lead are formed, which acting upon unchanged sulphide set free metallic lead as previously explained. The sulphide of sodium is of course also oxidized and converted ultimately into sulphate of soda. The results will obviously vary according to the mode of operation. If, for example, the mixture of galena and carbonate of soda be carefully roasted for some time with free access of air at a temperature below that at which carbonate of soda directly acts upon galena, oxide and sulphate of lead will be produced, and these when the temperature is raised sufficiently to cause the reaction just referred to will mutually reduce each other; but the carbonate of soda may decompose the sulphate of lead, forming sulphate of soda and setting free oxide of lead and carbonic acid.

It is stated that when sulphide of lead is heated with carbonate of potash, or with caustic soda or potash, the results are similar to those last described.

Sulphide of lead heated with the fixed alkalies or their carbonates and nitre, and alone with nitre or certain other oxidizing substances.—The addition of nitre in this case produces exactly the same effect upon the double sulphide of lead and alkaline metal at first formed as the oxygen of atmospheric air.[4] Berthier melted 100 parts by weight of galena with 300 of carbonate of soda, and then added 30 of nitre when

[2] Journ. of the Chem. Soc. antea cit. p. 48.
[3] Tr. des. Ess. 2. p. 671.
[4] Ibid. p. 672.

he obtained in a few moments 75 or 78 of lead. The same result as to reduction of lead occurs when a mixture of the three substances is directly melted; but in this case no alkaline sulphide is produced, all the sulphur being converted by the nitre into sulphuric acid, which remains in combination with alkaline base. By heating nitre alone with galena in the right proportion to acidify the sulphur of the latter, the lead is reduced; but, as Berthier remarks, active deflagration occurs which is apt to cause loss by projection, so that an accurate result cannot be calculated upon. Twice as much nitre is required as when alkaline carbonates are used in addition. If in this reaction nitrogen is evolved in the state of NO^4, then 102 parts by weight of nitre in round numbers will suffice to desulphurize 120 of sulphide of lead, as will appear from the following formula:—

$$KO,NO^5+PbS=KO,SO^3+Pb+NO^4.$$

When sulphide of lead is heated to bright redness in admixture with sulphate of soda partial reduction takes place, sulphurous acid escapes with effervescence, and sulphide of sodium is formed. In one experiment I found that galena mixed with 80% of dry sulphate of soda, yielded 29% of hard slightly malleable lead. The slag had been well melted, and when breathed upon it exhaled the odour of sulphuretted hydrogen. In another experiment galena heated in admixture with 66% of dry sulphate of soda yielded 58·6% of somewhat crystalline yet slightly malleable metal. In both experiments fumes were evolved during the heating.

Berthier states that sulphide of lead is reduced when heated with black oxide of manganese (MnO^2). Sulphurous acid escapes, and the product which has not been melted consists of metallic lead and protoxide of manganese.

$$PbS+2MnO^2=Pb+2MnO+SO^2.$$

Sulphide of lead heated with the fixed alkalies or their carbonates and carbon.—The reducing action of the fixed alkalies and of their carbonates is promoted by the presence of carbon. On this subject Berthier makes the following statement: Galena melted with four times its weight of black flux (*i.e.* calcined double tartrate of potash and soda) yields 75% of lead; with four times its weight of cream of tartar it yields 80%, the mass burning quietly with flame until the end of the operation; and heated with half its weight of carbonate of soda in a brasqued crucible it yields 74% or 75% of lead, accompanied with a reddish-grey slag containing very little sulphide of lead. Admitting that the effect of the carbon is to reduce or rather to prevent the formation of the equivalent of alkaline sulphate which appears in the equation previously given, whereby 4 equivalents of alkaline metal instead of 3 become available for reduction, that will not account for the much greater quantity of lead reduced than in the absence of carbon. But supposing that the alkaline base, say soda, is in the first instant reduced, and that sodium is thus brought in contact with sulphide

of lead, the latter would be instantly reduced with the formation of sulphide of sodium. If this supposition be correct it would follow that the compound of sulphide of lead and sulphide of sodium resulting from the direct action of carbonate of soda upon galena cannot exist when heated in contact with sodium, and that the former sulphide would in that case be reduced by the sodium.

Sulphide of lead heated with lime and with lime and carbon.—Jordan exposed galena imbedded in hydrate of lime in a carefully luted Hessian crucible during two hours to the temperature at which pig-iron begins to melt;[5] not a trace of reduced lead was observed, nor was the slightest odour of sulphuretted hydrogen perceived when diluted sulphuric acid was poured upon the lime after the experiment. The internal surface of the crucible near the cover was coated with crystallized sulphide of lead, and the lime covering the galena in the crucible was permeated with the same sulphide. Pattinson had previously tried the experiment of passing steam over galena at white-heat and then over lime in the same porcelain tube. The lime was permeated with galena, but there was no separation of lead. On heating a mixture of 6 parts by weight of galena, 12 of slaked lime and 3 of charcoal, as in the foregoing experiment, Jordan found that a very small quantity of lead was reduced, and that the lime in contact with it evolved sulphuretted hydrogen on the addition of dilute sulphuric acid.[6] The inner surface of the upper part of the crucible was coated with crystals of sublimed galena.

According to Berthier, when galena is heated with caustic lime in a brasqued crucible it is desulphurized, and the reduced lead occurs in shots in the slag, which consists of double sulphide of lime and lead and the lime in excess.[7]

Jordan made the converse experiment of heating, in a covered and carefully-luted Hessian crucible, a mixture of 6 parts by weight of lead, 4 of burnt gypsum (CaO,SO^3) and 1 of charcoal. Gypsum mixed with charcoal was put at the bottom of the crucible and pressed down, then the lead mixed by trituration with gypsum and charcoal, and at the top a mixture of gypsum and charcoal. The whole of the lead is stated to have been changed into sulphide. The inner surface of the crucible was lined with crystals of sulphide of lead and the gypsum at the bottom was permeated with the same sulphide; but the top layer of gypsum had the yellow colour of liver of lime (sulphide of calcium) and when breathed upon evolved sulphuretted hydrogen.[8]

Rivot states when an intimate mixture of galena and lime is heated to redness, with free access of atmospheric air, sulphate of lime is formed.[1]

Sulphide of lead heated with baryta and with baryta and carbon.—The results are the same as with lime, *mutatis mutandis*.[2]

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[5] Erdmann's Journ. 1831, 11. p. 333.
[6] Ibid. p. 334.
[7] Tr. des Ess. 2. p. 673.
[8] Op. cit. p. 344.

[1] Principes Généraux du Traitement des Minerais Métalliques, 2. p. 38.
[2] Berthier, Tr. des Ess. 2. p. 673.

Sulphide of lead heated with sesquioxide of iron.—There is no separation of metallic lead. The following experiment was made by Jordan. A mixture of 6 parts by weight of galena and 3 of red hæmatite, covered with a layer of hæmatite an inch thick, was strongly heated in a covered earthen crucible, but not the least trace of lead was separated. The sides of the crucible were coated with sublimed crystals of galena, and the hæmatite was thoroughly permeated with galena.[3] Berthier asserts that the oxide of iron is reduced to a lower degree of oxidation with the evolution of sulphurous acid, in which case some lead must be reduced;[4] but as this reduced lead may be oxidized by another portion of the higher oxide of iron, there may appear no separation of lead. He further asserts that blacksmith's iron-scales has no action on sulphide of lead.

Sulphide of lead heated with iron.—At a good red-heat complete reduction occurs with the formation of sulphide of iron. The temperature should at least be sufficient perfectly to melt the resulting sulphide of iron. In this country iron is the reducing agent generally employed in assaying galena, which is heated in an iron crucible. By this means it will be perceived that where the galena is hottest, namely, round the internal surface of the crucible, it is there in contact with the reducing agent. Iron is used as a reducing agent in lead-smelting; and for this purpose scrap wrought-iron, cast-iron or steel may be indiscriminately adopted. Cast-iron is much the best, because it melts at the temperature employed. Wrought-iron is very slow in its action in the smelting-furnace.

Nolte, of Clausthal, has experimented on the degree of reducing action exerted by iron in various proportions upon sulphide of lead. With this object he prepared sulphide of lead by heating a mixture of lead and sulphur, and re-melting the product with sulphur. It does not seem to have been analysed, but only assayed by the method practised in the Upper Harz; it yielded 80% of lead, which is considerably less than would be obtained in this country by a skilfully-conducted assay of pure sulphide of lead in an iron crucible. The iron used was in the state of filings previously heated to redness in admixture with 1% or 2% of charcoal in order to ensure the absence of oxide of iron. The mixture of sulphide of lead and iron-filings was put into an earthen crucible and covered with charcoal-dust and common salt in succession. The crucible was heated during 1¼ hour in an assay muffle, which, in order to raise the temperature as high as possible, was filled up with pieces of charcoal. In each experiment the same quantity of lead was operated upon, namely, 200 "assay-pounds,"[5] a quantity which seems very little for such experiments. Then it would probably have been better to have avoided the use of common salt. Every precaution seems to have been taken to exclude

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[3] Erdmann's Journ. 1831, 11. p. 2.

[4] Tr. des Ess. 2. p. 673.

[5] Probircentner = 100 Probirpfunds = 5 grammes = 76·5 grains. Therefore, 200 Probirpfunds (assay pounds) = 0·765 × 200 = 153 grains. Die Oberharzer Hüttenprocesse. Bruno Kerl. 1860, p. 200.

access of atmospheric air, which, by its oxidizing action on the sulphide of lead, would obviously be a source of error. Nolte's results are given in the following table:—

No.	Ratio of sulphide of lead to iron.	Parts by weight of sulphide of lead.	Parts by weight of iron.	Reduced lead.	Composition of regulus.			Total weight of regulus.	Weight of lead reduced for 1 part by weight of iron.
					Lead.	Iron.	Sulphur.		
I.	7PbS : Fe	100	2·5	...	86·5	2·5	13·5	102·5	...
II.	7PbS : Fe^2	100	5·0	9·0	77·5	5·0	13·5	96·0	1·8
III.	7PbS : Fe^3	100	7·5	22·0	64·5	7·5	13·5	85·5	2·9
IV.	7PbS : Fe^4	100	10·0	27·5	59·0	10·0	13·5	82·5	2·7
V.	7PbS : Fe^5	100	12·5	42·0	44·5	12·5	13·5	70·5	3·4
VI.	7PbS : Fe^6	100	15·0	48·0	38·5	15·0	13·5	67·0	3·2
VII.	PbS : Fe	100	17·5	54·5	32·0	17·5	13·5	63·0	3·1
VIII.	7PbS : Fe^8	100	20·0	60·0	26·5	20·0	13·5	60·0	3·0
IX.	7PbS : Fe^9	100	22·5	66·0	20·5	22·5	13·5	56·5	3·0
X.	7PbS : Fe^{10}	100	25·0	75·0	11·5	25·0	13·5	50·0	3·0
XI.	7PbS : Fe^{11}	100	27·5	78·5	8·0	27·5	13·5	49·0	2·8
XII.	7PbS : Fe^{12}	100	30·0	80·0	6·5	30·0	13·5	50·0	2·7
XIII.	7PbS : Fe^{13}	100	32·5	80·5	6·0	32·5	13·5	52·0	2·6
XIV.	PbS : Fe^2	100	35·0	80·0	6·5	35·0	13·5	55·0	2·3
XV.	7PbS : Fe^{15}	100	37·5	80·0	6·5	37·5	13·5	57·5	2·7
XVI.	7PbS : Fe^{16}	100	40·0	79·5	7·0	40·0	13·5	60·5	2·0
XVII.	7PbS : Fe^{17}	100	45·0	75·0	11·5	45·0	13·5	70·0	1·7
XVIII.	7PbS : Fe^{18}	100	50·0	76·0	10·5	50·0	13·5	74·0	1·5

In No. I. the reduced lead was so entangled in the regulus that its weight could not be determined. It has generally been admitted that the equation PbS+Fe=Pb+FeS correctly expresses the reaction which occurs in the reduction in question; but this view is not confirmed by the results of the experiments in the table from VII. to XI. inclusive, which lead to the inference that much more iron is required to reduce sulphide of lead than the received theory would indicate, and that the resulting regulus contains more iron than the protosulphide. In Nos. XII. to XVI. inclusive, the largest quantity of lead was reduced, the extremes being 79·5% and 80·5%. In a similar experiment long previously made by Fournet, the regulus obtained "was homogeneous and strongly magnetic; but by trituration it was partially reduced to powder and the rest was left in the form of small, white, malleable, metallic grains, which were only the iron in excess, mechanically retained in the regulus without having been even melted."[6] Fournet re-melted this regulus in a brasqued crucible at 150° Wedgwood's pyrometer: the product consisted of a granular, brass-yellow (bronze-yellow?) regulus like pure protosulphide of iron, and underneath of very brittle white cast-iron, of which the iron was supposed to have been derived from that existing in the metallic state in the regulus produced in the first fusion: the whole was enveloped in a very thin skin of malleable lead, which Fournet stated could only have been the product of the portion of metal that

[6] Ann. des Mines, 3. s. 4. p. 15.

had remained absorbed in the first regulus. Nos. XVII. and XVIII. would lead to the conclusion that with more than 40 parts by weight of iron for 100 of sulphide of lead there is sensible decrease in the quantity of lead reduced. In Nos. V., VI., and VII., most lead was reduced for 1 part of iron, the extremes being 3·4 and 3·1. In Nos. VII. and VIII., supposing no loss of lead to have taken place by volatilization, about $\frac{1}{3}$ of the sulphide of lead remained unreduced in the regulus, notwithstanding the iron used sufficed theoretically to effect complete reduction of the whole. Nolte suggests the following equation as approximately expressive of the reaction in these two experiments:—

$$3PbS+Fe^3 = Pb^2+(PbS+Fe^2S+FeS).$$

Nolte's mode of experimenting with iron in the state of filings is liable to the objection that the reduced lead may contain mechanically diffused iron, and in sufficient quantity materially to affect the accuracy of his results. This objection is not merely hypothetical, but is well founded on experience.

Sulphide of lead heated with oxide of iron and carbon.—As oxide of iron is quickly reduced to the metallic state when heated with carbon, it might have been anticipated that on heating a mixture of sulphide of lead, oxide of iron, and charcoal in sufficient proportion to combine with the oxygen of the latter, the whole of the lead would be set free; and experiments have proved this to be the fact. Jordan thus experimented upon mixtures of galena with red hæmatite and charcoal, and with hammer-slag or iron-scales and charcoal. In the latter case the yield of lead was a little less than in the former; but whether this difference depended on the duration of the process or upon the temperature, Jordan left undecided, though he was of opinion that energetic action due to high temperature is favourable to the yield of lead. When charcoal-finery iron-slag, which consists for the most part of basic silicate of protoxide of iron, was substituted by Jordan for oxide of iron in similar experiments, the result with respect to reduction of the sulphide of lead was least favourable.[7]

Sulphide of lead heated with tribasic silicate of protoxide of iron. ($3FeO,SiO^3$).—The silicate of protoxide of iron was prepared by heating an intimate mixture of very pure red hæmatite, sand, and anthracite-powder in the manner described in the second volume of this work on Iron and Steel: it contained 54·1% of iron, the theoretical quantity being 54·5%. The sulphide of lead was prepared by heating sulphur with lead reduced from red-lead: it contained 86·58% of lead, the theoretical quantity being 86·61%. A mixture of 500 grains of the silicate of protoxide of iron and 400 grains of the sulphide of lead, both in fine powder, was placed in an earthen crucible. This crucible with a cover luted on was put into another earthen crucible, the space between the two was filled with small pieces of charcoal, and a cover was luted on the second crucible. The mixture was thus ex-

[7] Erdmann's Journ. 1831, 11. p. 334.

posed for about 20 minutes to a high temperature, counting from the time when it was supposed the temperature sufficed to cause fusion. The crucibles were then taken out of the furnace and left to cool. The product consisted of three substances occurring in the following order from the top :—a layer of dark-coloured largely-crystalline slag somewhat metallic in lustre,—a layer of regulus which weighed 280 grains, —and a button of hard lead-like metal which weighed 30 grains. The slag and regulus were triturated to fine powder, and any iron which had been reduced in the latter was extracted by means of a magnet; they were then re-heated in a small crucible with the button of metal in the centre during the same time and at the same temperature as in the first instance. The product consisted of a layer of slag about an inch thick, which in appearance precisely resembled that of the first fusion, and weighed 475 grains,—of a layer of crystalline dark blueish-grey regulus which weighed 204 grains,—and of a button of metal, which weighed 76 grains. Hence considerable loss had occurred, exceeding what would result from the evolution of sulphurous acid, which was due probably to the volatilization of sulphide of lead at the high temperature employed. The regulus was composed as follows :—

Lead	66·95
Sulphur	17·57
Iron	15·69
	100·21

The composition may, therefore, be approximately represented by the formula PbS+FeS.

The slag was composed as follows :—

Protoxide of iron	63·99
Silica	35·79
	99·78

It contained only a trace of alumina, and its composition may, therefore, be approximately represented by the formula $2FeO,SiO^3$. The reaction may be expressed by the following equation :—

$$2(3FeO,SiO^3)+5PbS = 2(2FeO,SiO^3)+2(PbS,FeS)+SO^2+Pb^3.$$

A possible source of error in this experiment is reduction by carbonic oxide, though special precautions were taken as far as practicable to obviate such error. (By J. C. Cloud, in my laboratory.)

Sulphide of lead heated with tin.—The following experiment was made in my laboratory by Dick. Galena and tin were heated in the ratio PbS : 2Sn. The product was a well-melted button, consisting of two layers, which, though brittle, yielded somewhat under the hammer like talc. The upper layer was crystalline, dark-grey, and bright-metallic in lustre, much more brittle than the lower layer, and friable under a knife-edge. The lower layer could easily be cut with a knife; its fracture was so largely crystalline and foliated that the

cleavage planes extended through from top to bottom; the colour of this fracture was dark-grey, not blue like galena nor so black as graphite, but somewhat brownish, and the lustre was bright-metallic and suggestive of that of talc; it resembled protosulphide of tin artificially made by heating tin and sulphur together. Both layers much resembled each other in external character, but the line of separation between them was distinct, and they could easily be detached from each other. On removing a portion of the upper layer, towards the centre of the button, a little metallic lead was found interposed. The experiment has been repeated in my laboratory by Smith on a larger scale: the quantities operated upon were 3700 grains of galena and 3480 of tin. Fusion was effected in a covered black-lead crucible, the surface of the mixture having been previously covered with small pieces of charcoal. The crucible and contents were left to cool in the furnace during the night. The result was similar to that above recorded, except that at the bottom a small button of metal was found, in which was a cavity containing crystals.

Fournet heated mixtures of sulphide of lead and tin in the following ratios:—

I.—PbS : Sn.
II.—PbS : Sn^2.

No. I. melted at 50°, Wedgwood's pyrometer, with the production of blueish flame. After slow cooling the crucible was found to be cracked, in consequence, it was supposed, of the great increase in volume of the contents from crystallization. The product consisted of an upper layer crystallized in large plates, metallic in lustre, very bright, dark-grey or black, and not sectile with a knife; and of a lower layer "divided into angular parts by a portion of the sulphide above which had dissolved in it, as is the case with sulphide of tin;" this layer was easily cut with a knife, was silver-white, and behaved in assays of it like an alloy of lead and tin. Fournet inferred that the upper layer or regulus was a double sulphide of lead and tin, and the lower layer an alloy of these metals. No. II. gave a regulus supposed to consist of sulphide of tin and a metallic button of lead alloyed with tin. As the products in these experiments were not analysed quantitatively, the inferences of Fournet can only be regarded as conjectural.[8]

Sulphide of lead heated with copper.—According to Berthier, sulphide of lead is completely reduced when heated with copper; but, he adds, it often happens that a portion of copper escapes the action of the sulphide and mixes with the reduced lead.[9]

The following experiment was made by Dick in my laboratory. A mixture of galena and copper in the ratio PbS+Cu was heated in a covered crucible. The product was perfectly fused, and consisted of two layers, the upper one of brittle regulus having a fine-

[8] Ann. des Mines, 3. s. 4. p. 19.

[9] Tr. des Ess. 1. p. 670.

grained blueish-grey fracture; and the lower one of soft malleable lead, containing 0·88% of copper.

Galena and metallic copper (bean-shot) were heated together in the ratio of PbS : Cu^2. The quantities operated upon being 239 grains of galena and 126 grains of copper. The copper was placed at the bottom of an earthen crucible and covered with the galena, over which pieces of charcoal were placed and a cover luted on. The crucible was kept at a red-heat for 20 minutes, and left to cool slowly afterwards. The product consisted of a button of metal, and regulus. The button resembled lead in appearance; it weighed 198 grains and contained 10·25% of copper. The regulus was crystalline and dull blueish-grey; it weighed 162 grains, and was found to be composed as follows:—

Copper	67·5
Lead	13·5
Sulphur (by difference)	19·0
	100·0

The composition of this regulus may be approximately represented by the formula $8Cu^2S+PbS$. The total quantity of copper and lead computed from the proportion found in the button and in the regulus, slightly exceeds the quantity of those metals used in the experiment. The discrepancy is probably due to want of uniformity of composition in the button, or in the regulus, or in both. The experiment was repeated and with similar results, the button of metal weighing 197 grains and the regulus 163 grains. (J. C. Cloud, in my laboratory.)

In another experiment a stout strip of copper was placed in the centre of 1000 grains of galena contained in an earthen crucible, which was kept at a moderate red-heat during 20 minutes. At the end of that time the residual copper was withdrawn, and the contents of the crucible were poured into an ingot-mould. The button of lead was hard, and weighed 814 grains. The surface of the regulus, where it had been in contact with the mould, was covered with moss-copper; in the colour and structure of its fracture, the regulus resembled disulphide of copper. (J. C. Cloud, in my laboratory.)

Sulphide of lead heated with zinc.—Lead is reduced, but owing to the infusibility of the sulphide of zinc formed it seems scarcely possible to obtain experimental results even approximately correct. The product consists of a hard, dull, black, porous mass, in which sulphide of lead and globules of lead are entangled. Fournet found that no reaction occurred at incipient cherry-redness.[1]

The following experiment has been made in my laboratory by Smith. A mixture of zinc in fine powder and galena was made in the ratio of 5PbS : Zn. The quantities operated upon were 2400 grains of galena and 132 of zinc. The object of taking so large a proportion of galena was to insure the fusion of the mass, and so

[1] Ann. des Mines, 3. s. 4. p. 28.

obviate the difficulty which occurs when the product contains a large proportion of zinc and does not melt. The mixture was heated in a covered plumbago crucible, having been previously covered with a layer of small pieces of charcoal. The product was crystalline of a deeper grey colour and duller in lustre than galena. At the bottom was a button of lead in a cavity, in which were minute beautifully defined cubes, apparently of lead.

Sulphide of lead heated with antimony.—Berthier simply states that antimonio-sulphides are formed.[2] Fournet heated lead with common sulphide of antimony (SbS^3), and found the products resembled galena in one part and in the other antimony: there was no distinct line of demarcation between the two.[3]

Exp. (I.). Sulphide of lead was heated with antimony in the ratio of $3PbS : Sb$, the materials operated upon being 3585 grains of galena (which yielded 80% lead by dry assay in the iron crucible), and 1200 grains of antimony. The mixture, covered with pieces of charcoal, was heated pretty strongly for about 15 minutes in an earthen crucible with a cover luted on, after which the fire was allowed to go down and the crucible left to cool slowly in the furnace during the night. The metallic product presented numerous air-holes where it had been in contact with the crucible; it appeared to be pretty homogeneous throughout; it was hard, crumbling to powder under the knife; the fracture was largely crystalline, the cleavage-planes being granular in texture; its colour was blueish-grey. The loss in weight amounted to 875 grains. In order to ascertain whether there was any tendency to separation into two layers, the proportion of sulphur was determined in a portion taken from the top and in a portion of the same weight taken from the bottom: the top portion contained 11·018% and the bottom portion 10·902%. Hence it may be inferred that the product was practically homogeneous. The pieces of charcoal, which had been placed on the top of the mixture, were coated with crystals of galena.

Exp. (II.). Sulphide of lead was heated with antimony in the ratio of $3PbS : Sb^3$, the materials operated upon being 358·5 grains of galena (containing 80% of lead) and 360 grains of antimony. The experiment was conducted in exactly the same way as the last. The product was finely crystalline, less blue, harder and more brittle than that of Exp. (I.). The loss in weight amounted to 50 grains. Where the metal had been in contact with the crucible were numerous air-holes. The pieces of charcoal which had covered the mixture were coated with small crystals of galena. Hence it may be inferred that sulphide of lead is not reduced when heated with antimony. (Experiments (I.) (II.) by J. C. Cloud, in my laboratory.)

Sulphide of antimony heated with lead.—Exp. (I.). Sulphide of antimony was heated with metallic lead in the ratio of $SbS^3 : Pb^3$, the materials being 168 grains of liquated Borneo sulphide of antimony

[2] Tr. des Ess. 1. p. 670.

[3] Ann. des Mines, 3. s. 4. p. 238.

and 310 grains of granulated lead. The experiment was conducted in the same way as the preceding experiments. The mixture was kept melted for about 10 minutes, and afterwards left to cool slowly. The product showed no appearance of separation into layers; it was somewhat tough; and its fracture was crystalline and blueish-grey. The loss amounted to 57 grains.

Exp. (II.). The preceding experiment was repeated on a much larger scale, the quantities operated upon being 8400 grains of Borneo sulphide of antimony and 15,525 grains of granulated lead. The product was crystalline, and more largely so towards the top; it was whiter towards the bottom; but there was no appearance of separation into layers. The loss in weight amounted to 1200 grains. The upper part contained 12·528% of sulphur, and the lower 7·685%. (Experiments (I.) (II.) by J. C. Cloud, in my laboratory.)

Sulphide of arsenic heated with lead.—A single experiment is recorded by Fournet, in which he heated lead and realgar in the ratio of $AsS^2 : Pb^2$. The product was in part vesicular (*boursoufflé*) and studded with little characteristic cubes of galena.[4] The loss in weight in the mixture operated upon very little exceeded the total weight of arsenic in the sulphide, which would lead to the inference that the latter had been wholly reduced with the volatilization of its arsenic and the complete conversion of the lead into sulphide, thus:—

$$Pb^2 + AsS^2 = 2PbS + As.$$

Admitting such to have been the reaction, then it is reasonable to conclude that when sulphide of lead is heated with arsenic it will not suffer the least reduction.

Sulphide of lead heated with cyanide of potassium.—The greater part but not the whole of the sulphide is reduced with the formation of sulpho-cyanide of potassium, and the lead is separated in grains free from sulphur: there is also formed a black powder, which, on the addition of hydrochloric acid gives out a feeble odour of sulphuretted hydrogen. By several re-meltings with the cyanide, the whole of the lead may be obtained in the metallic state.[5]

Sulphide of lead heated with ferrocyanide of potassium.—When anhydrous ferrocyanide of potassium, K^2FeCy^3, is heated beyond its melting-point with exclusion of atmospheric air, it is resolved into nitrogen, which escapes with effervescence, and a mixture of cyanide of potassium and of iron combined, it is stated, with carbon. This separation of iron or of carbide of iron in a state of extremely fine division suggested to Levol the application of ferrocyanide of potassium as a reducing agent for sulphide of lead. On heating 100 parts by weight of pure sulphide of lead, artificially prepared, with 100 of anhydrous ferrocyanide of potassium, and 50 of cyanide, he obtained good results. In four experiments from 84% to 84·5% of lead was reduced, the

[4] Ann. des Mines, 3. s. 4. p. 243.

[5] Traité de Chim. Analyt. H. Rose, 1861, 2. p. 226.

total quantity in pure sulphide of lead being 86·6%.[6] It is not stated whether Levol ascertained that the reduced lead was free from iron.

In 1851, that is long anterior to the date of Levol's paper, preliminary experiments were made in my laboratory by Smith and myself on the use of ferrocyanide of potassium as a reducing agent for galena, and the investigation was afterwards completed by Smith alone. The following results are extracted from the 'Laboratory Journal,' November, 1851. Purest galena from the Harz was operated upon and the ferrocyanide of potassium was used both dry and crystallized. Much effervescence occurs during the process, and there may be notable loss in consequence. The best results obtained with the ferrocyanide alone in the proportion of K^2FeCy^3 : PbS, *i.e.* 1 equivalent of iron to 1 of sulphur, were as under. The ingredients were intimately mixed and heated in earthen crucibles:—

I.—Dry ferrocyanide 307 grains, and galena 200 grains.
II.—Crystallized „ 352 „ and „ 200 grains.

No. I. gave 76% and No. II. 77% of lead.

The following results were also obtained:—

III.—Dry ferrocyanide 350 grains and galena 200 grains. After effervescence had ceased, common salt was put into the crucible, and the heat was continued until its contents were perfectly melted. The lead, which was poured out into an ingot-mould, weighed 165·5 grains, *i.e.* 82·75%. It was found to contain 0·48% of iron.

IV.—Crystallized ferrocyanide 352 grains, and galena 200 grains. After effervescence had ceased, the crucible was allowed to cool, and when cold it was broken open. The lead was diffused through the mass in small globules. The product was re-melted with the addition of a small quantity of ferrocyanide and 200 grains of carbonate of soda, by which means a single button of lead was produced which weighed 165·5 grains, *i.e.* 82·75%.

V.—Crystallized ferrocyanide 400 grains, and galena 200 grains. After effervescence had ceased, common salt was added. The button of lead weighed 165 grains, *i.e.* 82·5%.

When the salt was previously mixed with the ferrocyanide and galena, much less lead was obtained, as shown by the following experiment:—

VI.—Crystallized ferrocyanide 352 grains, galena 200 grains, and common salt 200 grains. The button of lead weighed 153 grains, *i.e.* 76·5%. It contained 0·84% of iron.

Other experiments were made to ascertain the effect of substituting chloride of calcium and borax for common salt, but the results were unsatisfactory. Chloride of calcium produces a thick slag in which the reduced lead is diffused in globules.

VII.—Crystallized ferrocyanide 352 grains, galena 200 grains, and dried borax 200 grains. A thick slag is produced and a higher

[6] Ann. de Chim. et de Phys. 3. s. 46. p. 472, 1856.

temperature is required than when common salt is used. The button, together with as much as could be collected of the lead in globules, weighed 130 grains, *i.e.* 65%.

VIII.—Experiment VII. was repeated at a higher temperature. The slag was black, well melted and free from globules of lead. The button of lead weighed 130·5 grains, *i.e.* 65·25%.

Sulphide of lead mixed with chloride of sodium and roasted with access of air.—I made several experiments on this subject in the years 1849 and 1850, and the results are as follow. By cautiously roasting an intimate mixture of galena and common salt so as to prevent clotting, which quickly occurs if the temperature is raised too high, sulphate of soda is formed in considerable quantity, which may be dissolved out of the product with water, and by evaporation be obtained crystallized. By treating only 20 grains or so, say in the ratio of PbS : NaCl, of a mixture of the two substances in a porcelain capsule over a gas-flame, this result may be easily confirmed. The washed residue consists of chloride, sulphate and oxide of lead, with, it may be, a little undecomposed sulphide. If the mass is too strongly heated, especially at first, the odour of sulphurous acid is evolved; but on suitably lowering the temperature that odour will cease, and if the operation be properly conducted, it will not again be perceived; and after the lapse of a certain time, not even though the temperature be notably raised. After roasting during 2 or 3 hours, the product becomes somewhat pasty and yellow while hot, but ash-grey when cold.

The materials used in the following experiment were comparatively pure galena from Yorkshire, pulverized and passed through a sieve of 3600 holes in the square inch, and common salt dried and passed through the same sieve. Of the former 20 lbs. avoirdupois were intimately mixed with 10 lbs. of the latter, *i.e.* in the ratio PbS : NaCl. The mixture was roasted on a little flat-bedded reverberatory furnace built expressly for the purpose, atmospheric air having free access through an opening in the side. At first, owing to excess of caution, the temperature was kept too low, and after roasting during several hours the mixture still continued pulverulent, and was only a little paler in colour than at the beginning. The temperature was now raised, when the mixture became somewhat pasty and oxidation seemed to take place pretty rapidly, sulphurous acid was evolved but not copiously, and white vapour was observed to proceed from the mixture. On allowing the mixture to cool it clotted into small hard lumps, which on being re-heated immediately became so soft as to be easily broken up by simply passing a rabble over them. The roasting was continued during 6 hours and the furnace with its contents was then left to cool. On breaking some of the lumps they were found to contain particles of unchanged galena. On the next day the roasting was resumed and carried on uninterruptedly during the whole of that day and the night succeeding, at the end of which period the product was raked out of the furnace. It weighed 23 lbs., and as clotting had occurred, especially near the fire-bridge, a considerable quantity of

it remained firmly adherent to the bed and sides of the furnace. It was reduced to powder which was ash-grey.

1000 grains of this product were washed with lukewarm water, at first by decantation and afterwards on a filter. The solution came perfectly clear through the filter; and when the wash-water gave only a very slight precipitate with chloride of barium, a salt of lead began to pass through, which caused a white precipitate in the previously filtered solution. The washing was then discontinued. By evaporation of the solution, a crop of characteristic crystals of sulphate of soda was deposited, which weighed 255 grains. The roasted product contained of

Dry sulphate of soda	15·96%
Chloride of lead	13·76%
Sulphate of lead	21·04%

In another similar very small experiment, in which only 20 grains of a mixture of galena and common salt in the same ratio, PbS : NaCl, as in the foregoing experiment, was very carefully roasted during 2 or 3 hours in a porcelain capsule, the product gave 16% of dry sulphate of soda and 29·0% of chloride of lead. In this experiment the temperature was under perfect control and was most carefully regulated; and there was no emission of white vapour at any time as in the preceding experiment. That vapour was probably chloride of lead; and this may probably account, at least in part, for the much greater quantity of chloride of lead in the latter case than in the former. However, both experiments should merely be regarded as tentative and the quantitative determinations in both as only approximate.

Sulphide of lead heated with chloride of ammonium.—A mixture of 300 grains of galena in fine powder, and 200 grains of chloride of ammonium, was heated moderately in an earthen crucible, and when complete fusion seemed to have occurred, the crucible was taken out of the furnace and left to cool slowly. While the crucible remained in the furnace, white fumes continually escaped from it. The product weighed 254 grains; its fracture presented cubical facets like those of galena; the prevailing colour of the mass was blackish; and by the action of water 40·25% of soluble matter was removed, The insoluble residue resembled unchanged galena. The composition of the soluble portion was found to be as follows:—

Lead	70·02
Chlorine	25·91
Sulphur	0·47
Ammonia (by difference)	3·60
	100·00

The lead and chlorine are nearly in the same ratio as in chloride of lead. (By J. C. Cloud, in my laboratory.)

LEAD AND CARBON.

Carbide of Lead.

The existence of such a compound was admitted by Berzelius, who prescribed two methods for its preparation, namely, the calcination of an intimate mixture of protoxide of lead and charcoal in a covered crucible, and the heating of cyanide of lead in a close vessel. He stated, moreover, that "carbon combines easily with lead at the moment the latter is reduced."[1] I have not found recorded any analytical or other evidence to show that the products thus obtained were anything more than mixtures of finely-divided lead and carbon; and so far as my own experience goes, I have seen no reason for supposing that lead combines even with a trace of carbon when the two elements are heated together either at low or high temperatures. John announced in 1820, that by heating lead and charcoal together, carbide of lead was sublimed in black spangles having a metallic lustre.[2] If I err not, no other person has obtained the like result. Until more satisfactory proof is adduced of the possibility of forming carbide of lead than what has been hitherto published, its existence cannot be admitted.

Carbonates of Protoxide of Lead.

When lead is subjected at ordinary temperatures to the combined action of oxygen, carbonic acid and water, whether in the state of vapour or liquid, a white hydrated carbonate of protoxide of lead is formed. Thus lead by long exposure to the atmosphere becomes coated with such a carbonate. This change may be well observed on the crystals of lead produced in Pattinson's process, which have been kept for some years as specimens at the Museum in Jermyn Street with no greater atmospheric exposure than in closed cases.

The incrustation on ancient Roman pig-lead, which is firmly adherent, is the product of the same atmospheric or weathering action. Some years ago a copious supply of singular objects of lead, termed "Pilgrims' signs," were alleged to have been extracted from the mud of the Thames and sold as genuine antiquities by a dealer. They were proved to be forgeries, and to the dealer was imputed knowledge of the fact, though in the sequel it appeared that he was as much imposed upon as his customers. A trial for libel ensued, and the plaintiff was nonsuited. The objects in question had been artificially coated with a greyish-white substance in order to imitate the crust of antiquity. The artificial coat could be easily washed off with water, and was found to contain nitric acid; whereas the genuine old crust could not be so removed, and contained carbonic, but no nitric, acid.

When lead is kept in distilled water with free access of atmospheric air, a flakey-white crystalline substance is produced, and after about a month the small crystals of anhydrous protoxide of lead pre-

[1] Tr. de Chim. 1846, 2. p. 591.

[2] Gmelin's Handbook, v. p. 122.

viously described, make their appearance in addition. According to Colonel Yorke,[3] the composition of the white substance may be expressed by the formula $2PbO,CO^2+HO$. It is termed dicarbonate by Gmelin.

WHITE-LEAD, CERUSE, FLAKE-WHITE.—The common white pigment, white-lead, is generally admitted to have the formula

$$3PbO,2CO^2+HO, \text{ or}$$
$$2(PbO,CO^2)+PbO,HO.$$

It is a white, amorphous powder. Many years ago I was a frequent visitor at white-lead works where novel processes were in operation, which came to an untimely end; and I well recollect how much I was impressed at seeing showboards in the counting-houses presenting sample patches of white-lead paint from those works; and how clearly each manufacturer thereby demonstrated the superiority of his own product. In the instances here referred to, there was self-deception, not imposition. Inventors, like fond parents, are slow to detect and acknowledge the faults of their own offspring. Although the manufacture of white-lead is not a branch of metallurgy, and therefore not a subject for description in this work, yet it may be well not wholly to pass it over without notice. The original Dutch process still holds its ground in this country, notwithstanding the numerous attempts to supersede it; and it seems certain that no other method has yielded a better article or a better financial result. The principle of this process is exposing lead to the combined action of acetic acid, atmospheric oxygen, carbonic acid, aqueous vapour, and a gentle heat. For this purpose earthen pots glazed internally are employed, which are usually of two sizes. The larger are contracted towards the bottom; but the smaller are either cylindrical or widen gradually towards the mouth. The acetic acid used is very dilute. The lead is cast at a low temperature into plates, or into trellis-like pieces. Acetic acid is put into the contracted portion of the larger pots and a coil of lead in the upper portion; whereas the smaller pots are only used as receptacles of acetic acid. The two kinds of pots are arranged at regular intervals, several rows of the smaller pots being placed between every two consecutive rows of the larger, thus leaving considerable space from the level of the tops of the larger to the level of the tops of the smaller pots. In this space the trellis-like pieces or plates of lead are piled, resting on the tops of the smaller pots, space enough being left between the upper surface of the lead thus piled and the level of the mouths of the larger pots, in order to allow of the considerable increase of bulk which occurs when lead is converted into white-lead. The process is effected in large rectangular chambers of brick or stonework. A layer of tanner's spent bark or stable litter, about 1 foot thick, is spread evenly over the bottom, and upon this layer the pots and lead are stacked as above described. A flooring of wooden planks about $1\frac{1}{2}$ inch thick, is laid over the whole so as to be

[3] Phil. Mag. 1834, 5. p. 85.

entirely supported by the taller pots. On this floor another layer of spent bark or litter about 1 foot thick is evenly spread, then a second layer of pots and planks, and so in succession until the chamber is filled, a layer of bark or litter being always at the top. Such a chamber is termed a "stack," and a stack may contain from 20 to 50 tons of metallic lead. In the course of from 2 to 4 months, the stack is taken down, when the lead will be found changed for the most part into white-lead, which is subjected to the operations of grinding, washing, levigating, and drying. When dry, it is packed in casks, and in that state is pure white-lead. When ground up with oil into paint, it may be mixed with variable quantities of sulphate of baryta, so as to produce the different kinds of commercial white-lead paint. The goodness of quality and price are proportionate to the quantity of pure white-lead. As a general rule it may be stated that the purer the metallic lead operated upon the better the quality of the white-lead produced. Other substances besides sulphate of baryta, such as chalk or gypsum, are occasionally used in the manufacture of certain qualities of paint.

It will be perceived that in a white-lead stack, the conditions previously stated to be essential for the formation of white-lead are fully attained. Atmospheric air slowly permeates every part of the mass; oxygen is thus supplied for the oxidation of the lead; carbonic acid is evolved from the bark or litter, and by oxidation of the lead and probably of some of the organic constituents of the bark or litter, the necessary heat is developed.

'At Clichy, near Paris, white-lead has long been manufactured by Thénard's method, which consists in passing carbonic acid through a solution of basic acetate of lead. Mr. Sewell, of Nottingham, about 35 years ago, made white-lead by passing carbonic acid through an aqueous solution of neutral acetate or sugar of lead mixed with a large excess of litharge, and he washed the precipitated white-lead by forcing water through it by means of a hydraulic press. I saw this process in operation. Messrs. Benson and Gossage passed the gaseous product of the most perfect combustion practicable of coke over layers of litharge mixed with a small proportion of sugar of lead. Costly and ingenious apparatus was employed, which seemed well to answer its purpose. I also frequently saw this process in operation. Another method was to subject granulated lead in revolving barrels to the combined action of atmospheric oxygen, carbonic acid and water.[4] By thus treating granulated lead without carbonic acid dense hydrated protoxide of lead was pretty quickly formed, a specimen of which I have seen.

Whatever process may be adopted for the manufacture of white-lead, it is obviously desirable to introduce as much carbonic acid as possible, or what is the same thing, to form as little hydrate of protoxide as possible, provided the quality of the product and conse-

[4] This process seems to have been tried several times on the large scale. See Wagner's Jahresber. 1860, 6. p. 268.

quently its commercial value be not thereby deteriorated. It appears that in the Dutch process the composition of the product may vary considerably with respect to the proportion of hydrate not only in the same stack but in different parts of the same layer. Mr. J. A. Phillips, who has had practical acquaintance with white-lead works, found that the composition of various samples of white-lead which he analysed after drying at 100° C., might be represented by the following formulæ :—

$$2(PbO,CO^2)+PbO,HO$$
$$3(PbO,CO^2)+PbO,HO$$
$$5(PbO,CO^2)+PbO,HO.$$

Under the microscope not one of these samples appeared in the least degree crystalline in structure.[5] According to Mr. J. A. Phillips, white-lead loses the whole of its chemically combined water at 150° C., and towards 170° C. its carbonic acid.[6] What has been stated respecting the reduction of oxides of lead applies equally to the carbonates. When white-lead is calcined with free access of air at the temperature of a red-lead oven it is changed into the variety of red-lead termed orange-lead, or, in commerce, orange-mine, on account of its tint. Commercial red-lead varies in tint from purplish to orange in proportion to its fineness of division; and white-lead produces the orange variety of red-lead simply because the protoxide of lead which it yields is in finer powder than what is produced from metallic lead in the first stage of its conversion into red-lead.

NEUTRAL CARBONATE OF PROTOXIDE OF LEAD. MONOCARBONATE. WHITE-LEAD ORE. CERUSSITE. PbO,CO^2.—It crystallizes in the prismatic system. It is precipitated as a white powder by passing carbonic acid to *saturation* through an aqueous solution of basic acetate of protoxide of lead,[7] or by the addition of excess either of carbonate of ammonia, of potash, or of soda to a cold aqueous solution of nitrate or acetate of protoxide of lead. Care must be taken to avoid heat, as in that case an alkaline carbonate throws down hydrated carbonate of protoxide of lead of the formula $2(PbO,CO^2)+PbO,HO$.[8] One part by weight of the monocarbonate dissolves in 50,550 parts of pure *boiled* water,[9] and in 7144 parts of water saturated with carbonic acid.[1] Colonel Yorke found that water, which contained carbonic acid in such proportion that when boiled it gave off $\frac{2}{3}$ of its volume of carbonic acid gas, dissolves from about $\frac{1}{50000}$ to $\frac{1}{60000}$ of protoxide of lead in the state of carbonate prepared by passing carbonic acid through an aqueous solution of basic acetate of lead.[2] All the compounds of the protoxide of lead, carbonic acid and water are changed into anhydrous monocarbonate by the action of carbonic acid sufficiently prolonged. All carbonates of lead are completely decomposed at a

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[5] Liebig u. Kopp's Jahresb. 1851, p. 357.
[6] Ibid. p. 695.
[7] Berzelius, Tr. de Chim. 4. p. 91.
[8] Lefort, Gmelin's Handb. 5. p. 126.
[9] Fresenius, Anleitung zur quantitativ. chemisch. Analyse, 1859, p. 143.
[1] Lassaigne, Berzelius' Jahresb. 1850, 29. p. 133.
[2] Phil. Mag. 1834, 5. p. 91.

temperature far below the melting-point even of lead, pure protoxide of lead remaining as the product.

The native monocarbonate or cerussite is not seldom found associated with galena, from which in some cases it may be derived by atmospheric oxidation; but then sulphate of lead must first be formed, and that salt would be quickly changed into cerussite by the action of water charged with bicarbonate of lime, gypsum resulting as an accessory product. As galena frequently occurs in limestone, it is not difficult to understand how in lodes occasionally it should be exposed to the combined influence of atmospheric air and such a solution of bicarbonate of lime, which, I find, immediately changes artificially precipitated sulphate of lead into carbonate.

LEAD AND ARSENIC.

Arsenide of Lead.

Lead when molten readily alloys with metallic arsenic, and the same result takes place when arsenious acid, AsO^3, is brought in contact with red-hot molten lead. By the latter method such an alloy is produced for the manufacture of lead shot, and is technically known as "temper." It is prepared by immersing arsenical glass under a bell-shaped cast-iron vessel in liquid lead heated to low redness. In this case protoxide of lead is formed, or, according to Berzelius, arseniate of protoxide of lead, either of which may be completely deprived of oxygen by throwing charcoal on the arsenical alloy while melted. A small quantity of this alloy is added to the molten lead intended to be cast into shot, as it tends to render the globules more spherical. When molten, arsenical lead is very liquid like mercury; arsenic hardens lead, lessens its malleability, and gives to it a crystalline dark-grey fracture. According to Berthier arseniuretted lead cannot at a white-heat retain more than 15·5% of arsenic, which corresponds exactly to an alloy of the formula Pb^4As. This alloy, it is stated, supports the highest temperature without loss of weight;[1] but Fournet, on the contrary, asserts that at 50° Wedgwood's pyrometer arseniuretted lead is wholly deprived of arsenic, which in volatilizing carries off some lead.[2] Berthier also states that at a sufficiently high temperature lead is wholly freed from arsenic by iron with the production of arsenide of iron; that litharge in excess converts the arsenic into arsenious acid which remains in combination with protoxide of lead; but that no change is caused by the addition of alkaline carbonates. Nickel and cobalt should act like iron upon arseniuretted lead.

The following experiments on this subject have been made by J. C. Cloud, in my laboratory. Granulated lead of remarkable purity and metallic arsenic were operated on. Earthen vessels were used, the mixtures were heated under a layer of anthracite powder, and the alloys were cast into ingots.

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[1] Berthier, Tr. des Ess. 2. p. 682.

[2] Ann. des Mines, 3. s. 7. p. 1835.

(I.) The mixture consisted of 1000 grains of granulated lead, and an equal weight of metallic arsenic. A fusible alloy was formed, which, when perfectly liquid, was poured into an ingot-mould. The alloy was very brittle, and broke under a single blow from a hammer; the fracture was crystalline, and of a dark steel-grey colour, which in a short time changed to brown by tarnishing, and in the course of about two days became nearly black. The alloy contained 20·73% of arsenic, and its composition may, therefore, be approximately represented by the formula Pb^5As.

(II.) The mixture consisted of 1000 grains of lead and 10 grains of metallic arsenic. The alloy, after having been slightly nicked across, broke under a single blow from a hammer; the fracture was finely crystalline, somewhat like that of cast-steel, slightly uneven, blueish-grey, and rather dull in lustre; the metal could be slightly scratched with the finger-nail.

(III.) The mixture consisted of 1000 grains of lead and 5 grains of metallic arsenic. The ingot broke in the vice after bending twice. The fracture was uneven, lighter coloured than that of the alloy in Exp. II., and the metal was also much softer.

(IV.) The mixture consisted of 1000 grains of lead and 1 grain of arsenic. The alloy resembled ordinary lead in appearance.

(V.) 1000 grains of lead were kept melted under anthracite powder in a crucible, while 2000 grains of metallic arsenic were gradually added and stirred in. The addition of the arsenic seemed to reduce the temperature of the lead considerably. After the whole of the arsenic had been added, the temperature was raised so as to ensure complete liquidity of the alloy, which was then poured into an ingot-mould. The ingot weighed 1600 grains; it was brittle; its fracture was largely crystalline and dark steel-grey, tarnishing very quickly. The alloy was found to contain 38·55% of arsenic, so that its composition may be approximately represented by the formula PbAs.

(VI.) In this experiment arsenious acid was substituted for metallic arsenic, and the covering of anthracite powder was omitted. On the top of 1000 grains of molten lead, in a clay crucible, were placed 320 grains of arsenious acid, over which a smaller crucible was kept inverted. When the metal was in tranquil fusion, the contents of the crucible were poured into an ingot-mould. The ingot was hard and brittle; the fracture was fine-grained and of a steel-grey colour, and tarnished rapidly; it was accompanied by a semi-opaque, amber-coloured glassy product. This result confirms the accuracy of the statement that molten lead partially reduces arsenious acid with the formation of an oxidised arsenical compound of lead and arsenic.

Quantity of arsenic in shot.—This has been determined by Smith in my laboratory in the case of two samples of shot, bought at different shops in London (A.D. 1870). One sold as "No 1." $\frac{1}{6}$″ in diameter, contained 0·133% of arsenic and 0·030% of copper; and the other, sold as "No. 6," $\frac{1}{8}$″ in diameter, contained 0·1157 of arsenic and 0·284% of copper. In the analysis of each sample 2000 grains were operated upon.

Arsenites of Protoxide of Lead.

Two salts have been described of the formulæ PbO,AsO^3 and $2PbO,AsO^3$. They both contain combined water, the proportion of which does not seem to have been determined. Arsenite of ammonia throws down the first from a solution of acetate or sugar of lead, and the second from a solution of basic acetate of lead. Thus prepared both occur as white powders, fusible by heat into anhydrous yellow glasses, which when rubbed become strongly electric.[3] The substances obtained by melting various mixtures of protoxide of lead and arsenious acid have been described at p. 18 of this volume. It is stated that the vapour of arsenious acid is rapidly absorbed by heated protoxide of lead, which becomes red-hot and melts, and that when cold the product is a sulphur-coloured enamel or glass, easily fusible and undecomposable at a bright red-heat.[4] The properties of these arsenites have not been satisfactorily investigated.

Arseniates of Protoxide of Lead.

Two arseniates are known of the formulæ $2PbO,AsO^5$ and $3PbO,AsO^5$. The first is precipitated as a white powder by the addition of arsenic acid, or by gradually dropping a solution of an alkaline diarseniate into a solution of mononitrate of protoxide of lead, taking care to leave the latter in excess: it fuses easily. The second is thrown down as a white powder by the addition of diarseniate of soda in excess to an aqueous solution of a salt of lead: at low redness it acquires a transient yellow colour without even sintering: it melts at a higher temperature than the preceding salt.[5] The products obtained by melting various mixtures of protoxide of lead and arsenic acid have been described at p. 18 of this volume. Berzelius remarks that the affinity of arsenic acid for protoxide of lead is so great that when a neutral arseniate is mixed with acetate or sugar of lead a subarseniate of lead is thrown down and acetic acid is set free.

The arsenites and arseniates of protoxide of lead are either insoluble, or very nearly so, in water, but soluble in nitric or hydrochloric acid and in solution of caustic potash or soda. They are completely decomposed when heated with excess of fixed alkaline carbonate, alkaline arsenite or arseniate being respectively formed. They are all easily reduced to arsenides when heated with excess of charcoal or black-flux; but Berthier states that when only a small quantity of reducing agent is added pure lead is alone separated. The same observer asserts that arsenides of lead are decomposed when heated either with arseniates or arsenites of lead, the arsenic of the arsenide being converted by the oxide of lead of the salts into arsenious acid, which volatilizes.[6] As might be anticipated, arseni-

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[3] Berzelius, Tr. de Chim. 4. p. 108.
[4] Simon, Gmelin's Handb. 5. p. 173.
[5] Berzelius, Tr. de Chim. 5. p. 107. Gmelin's Handb. 5. p. 173. Scheele's Essays: London, 1786, p. 179.
[6] Tr. des Ess. 2. p. 683.

ates of protoxide of lead form fusible mixtures with silicates of that oxide.[7] The acid, both of arsenites and arseniates of protoxide of lead, should be wholly displaced by a due proportion of silica at a temperature sufficient to form silicate of protoxide of lead, arsenious acid being evolved in the first case, and arsenious acid and oxygen in the second.

Arseniate of Protoxide of Lead combined with Chloride of Lead.

Native arseniate of lead or mimetesite is a double salt of this nature, its formula being

$$3(3PbO,AsO^5)+PbCl.$$

LEAD AND PHOSPHORUS.

Phosphide of Lead.

More than eighty years ago Pelletier published his interesting researches on metallic phosphides, which are well worth reading even at the present day. He dropped phosphorus upon molten lead until the metal seemed to him to be saturated with it, and he observed that during the process a little phosphorus burned and was converted into phosphoric acid, which combined with a little oxide of lead also formed at the same time, the product being a milky-white glass which adhered to the crucible. This phosphide of lead gave off its phosphorus when melted before the blowpipe. He prepared phosphide of lead by heating the dry residue of evaporated urine mixed with chloride of lead. The phosphide was found in the state of small bright grains in the carbonized mass, which were easily separated by washing and melted into one button. The metal, however, was pasty while molten and evolved phosphorus, which burned at the surface with the production of white fumes of phosphoric acid. Pelletier thought that the phosphide thus procured might contain from 12% to 15% of phosphorus, or more than the phosphide prepared by any other method. He heated 4 ounces of glacial or vitreous phosphoric acid with an equal weight of lead-filings, and got a somewhat blueish silver-white metallic button weighing 3 ounces, which quickly tarnished in the air, could be cut with a knife, but when struck upon an anvil separated into laminæ.[1] As no carbonaceous matter was used in this experiment, it may be inferred that lead is able to reduce phosphoric acid at a high temperature. The correctness of this inference has been confirmed by J. C. Cloud in my laboratory. Lead and glacial phosphoric acid were strongly heated together in a covered clay crucible, when phosphorus was evolved in considerable quantity, which ignited when it came in contact with the air. The metal was poured into an ingot-mould before the phosphorus ceased to burn. The ingot contained numerous cavities, and

[7] Tr. des Ess. 2. p. 683.

[1] Annales de Chimie, 1792, 13. p. 114.

smelt strongly of phosphorus; but on examining a portion free from cavities, not a trace of phosphorus was found in it. There was a glassy slag, of which the colour passed gradually from dark greyish-blue at the top into white at the bottom: it was substantially phosphate of lead. By dropping phosphorus upon molten lead Landgrebe did not succeed in introducing more than 3% into the metal. The product resembled pure lead in appearance.[2] This subject has also been examined in my laboratory by J. C. Cloud. Amorphous phosphorus was added in small portions successively to molten lead covered with anthracite powder in a crucible, and the contents were well stirred. The metal was poured into an open ingot-mould, and just before it solidified, innumerable jets of burning phosphorus appeared on its surface. After solidification and cooling, the metal was found to be somewhat vesicular, and to smell strongly of phosphorus. A portion of the metal free from air-holes was carefully tested for phosphorus, but none was detected. The foregoing experiment was repeated, and with the same result. Hence it appears that any phosphorus which may be absorbed by molten lead is wholly evolved during solidification; and it will be shewn hereafter that a like result occurs with silver.

When phosphuretted hydrogen is passed through a solution of a salt of lead, a brown precipitate is slowly formed, which before the oxidizing flame of the blowpipe is converted into crystalline basic phosphate without loss of phosphorus.[3]

Phosphates of Protoxide of Lead.

Salts have been described of the following formulæ:—

I.—$3PbO+PO^5$.
II.—$2PbO,HO+PO^5$ (dried at 100° C.).
III.— $PbO+PO^5$.

No. I. is precipitated as a white amorphous powder by the addition of tribasic or common phosphate of soda to a solution of acetate or sugar of lead, the acetate being in excess: in this case the supernatant liquor will contain free acetic acid. It melts before the blowpipe, and the surface of the bead when cold presents bright crystalline facets. No. II. is thrown down as a bulky white powder by the addition of bibasic or pyrophosphate of soda to a solution of nitrate of protoxide of lead in excess. No. III. subsides as a white crystalline precipitate shortly after mixing a dilute solution of monobasic or metaphosphate of soda with a solution of nitrate of protoxide of lead in excess: it contains a little nitrate of lead. It melts at a red-heat without intumescence and solidifies on cooling into a transparent glass.[4]

All these phosphates are insoluble in water and soluble in dilute

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[2] Berzelius, Jahresb. 1830, 9. p. 135.
[3] H. Rose, Berzelius, Jahresb. 1834, 13. p. 87.
[4] Vide Handwörterb. der reinen u. angewandt. Chemie, 1854, 6. pp. 348, 390, 409.

nitric acid and in a solution of caustic potash or soda. The whole of the lead, or nearly so, is separated in a state of purity when they are strongly heated in admixture with charcoal, thus :—

$$3PbO,PO^5+C^8=Pb^3+8CO+P.$$

According to Berthier, No. III. is not reduced when heated to whiteness in a brasqued crucible, or at most its surface where in contact with the carbonaceous lining only becomes coated with a skin of metal; but at 150° Wedgwood it is in great part reduced.

The following experiments on the reduction of this phosphate of lead by charcoal have been made in my laboratory. A mixture of 300 grains of the phosphate and 40 grains of charcoal was heated in a covered clay crucible. A high temperature was needed for perfect fusion. The metal was poured into an ingot-mould. The ingot weighed 223 grains, was very soft and malleable, and did not contain any phosphorus. This number corresponds to 74·3% of lead in the phosphate, whereas the theoretical quantity is 76·5%. The foregoing experiment was repeated, and the proportion of lead obtained was 75·9% of the phosphate. This lead was also carefully tested for phosphorus, but none could be detected in it. The conclusion from these experiments is that this phosphate of lead is wholly reduced by charcoal at a strong heat.

Phosphates of lead are readily and completely reduced when heated with iron or a mixture of oxide of iron and charcoal in excess, phosphide of iron being formed. They are easily reduced by black-flux, with the formation of alkaline phosphate. Their reduction by charcoal is not promoted by the presence of boracic acid: a mixture of No. III. and this acid in the proportion of 30%, was found by Berthier to melt in a brasqued crucible into transparent very brilliant topaz-yellow glass. The same observer states that No. III. exerts no action upon galena at any temperature, and that the product obtained by melting these two substances together is homogeneous and more or less deep grey.[5] This point has been examined by J. C. Cloud in my laboratory. A mixture of 119·5 grains of galena and 182·5 grains of phosphate of lead was heated in a covered crucible which was left to cool slowly. The contents of the crucible consisted of two layers, the upper one of phosphate of lead which was crystalline, dull and of a dirty green colour, and the lower one of galena, which had lost only 8 grains. The experiment was repeated and with the same result. The statement, therefore, of Berthier that there is no reaction between phosphate and sulphide of lead at a high temperature is confirmed by these experiments. Phosphates of lead should be completely reduced when strongly heated with a suitable mixture of lime, fluor-spar, and carbonaceous matter, a fusible slag composed of phosphate of lime and fluor-spar being formed.

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[5] Tr. des Ess. 2. pp. 681, 682.

Phosphate of Protoxide of Lead combined with Chloride of Lead.

The so-called native phosphate of lead is a double salt of this nature, its formula being

$$3(3PbO,PO^5)+PbCl.$$

It may be prepared artificially by adding a boiling solution of chloride of lead to a boiling solution of common phosphate of soda, keeping the latter in excess, and then boiling the mixture for some time. The product is insoluble in water, but soluble in dilute nitric acid. It melts before the blowpipe, and the bead crystallizes on cooling, with momentary incandescence. If the conditions of the process be reversed and the solution of phosphate of soda be added to the solution of chloride of lead, the latter being kept in excess, the precipitate has the formula $2(3PbO,PO^5)+PbCl$. It is similar in appearance to the preceding salt, and when strongly heated it is changed into that salt with the loss of part of its chloride of lead.[6] Some varieties of natural pyromorphite contain between 2% and 3% of arsenic acid, and others phosphate of lime with fluoride of calcium.[7] Other varieties again are isomorphous mixtures of mimetesite and pyromorphite, of which the composition may be represented by the formula

$$3\left(3PbO\left\{\begin{matrix}AsO^5\\PO^5\end{matrix}\right.\right)+PbCl.$$

The composition of a variety from Arqueros in Chili and from Långbanshytta in Sweden may, according to Rammelsberg, be represented by the formula [8]

$$3\left(3\left\{\begin{matrix}\frac{3}{4}PbO\\\frac{1}{4}CaO\end{matrix}\right\}\left\{\begin{matrix}\frac{2}{3}AsO^5\\\frac{1}{3}PO^5\end{matrix}\right.\right)+PbCl.$$

LEAD AND CHLORINE.

Chloride of Lead.

PbCl.—It has been found crystallized at Vesuvius, and is termed Cotunnite by mineralogists. It is formed without incandescence by the direct action of chlorine on lead; by boiling hydrochloric acid with lead, when hydrogen is evolved; and by the combined action of hydrochloric acid and atmospheric air upon lead at ordinary temperature; but it is only very slowly produced by any of these methods, especially the first and last. It may be conveniently prepared by digesting protoxide of lead with excess of hydrochloric acid, or by the addition of that acid or of various soluble chlorides to an aqueous solution of a salt of lead, such as nitrate or acetate, when it is precipitated as white crystalline powder. Hydrochloric

[6] Handwörterb. der Chem. 1854, 6. p. 349.
[7] Rammelsberg, Handb. der Mineralchem. 1860, p. 356. [8] Op. cit. p. 383, 384.

acid converts red-lead into chloride of lead, with the evolution of chlorine, thus :—

$$Pb^3O^4 + 4HCl = 3PbCl + 4HO + Cl.$$

It may also be made by digesting galena with hydrochloric acid, when sulphuretted hydrogen is disengaged, and it is thus produced on a large scale in the first stage of the manufacture of the pigment known as "Pattinson's Oxychloride of Lead." When deposited on the cooling of a hot solution it occurs in characteristic white acicular crystals and in thin plates. It dissolves in about 30 parts of water at 100° C., and in 135 parts at 12·5° C. Mr. Pattinson informed me (1851) that he found it to dissolve in 32 parts of water at 100° C., and in 126 at 12·7° C. It is in great measure precipitated by the addition of hydrochloric acid or chloride of calcium from its aqueous solution; water acidulated with hydrochloric acid dissolves $\frac{1}{46\frac{1}{3}6}$ of its weight of chloride of lead, and a dilute aqueous solution of chloride of calcium $\frac{1}{3\frac{1}{3}4}$: strong hydrochloric acid, especially when hot, copiously dissolves chloride of lead, which is thrown down on the addition of water. It melts below redness into a thin liquid, which neither runs through nor corrodes earthen crucibles, and which on cooling becomes a white, horn-like, translucent substance, having a specific gravity of 5·6824, termed by the old chemists *plumbum corneum*, or horn-lead.[1] At a red-heat it sublimes, and if there be free access of air, it is only partially volatilized with the production of thick white pungent smoke, and yellow oxychloride of lead. It may be reduced by heating it in admixture with lime and charcoal, and the reaction which occurs is shown in the following equation :—

$$2PbCl + 2CaO + C = Pb^2 + 2CaCl + CO^2.$$

The mixture should be intimate and the temperature bright redness; but if the experiment be not carefully conducted much loss of lead may result from the volatilization of chloride of lead. In operating upon not more than 35 grains of chloride of lead, I obtained a button of soft lead weighing 22 grains, so that there was a loss of about 14% of lead, but a portion of this was found in the slag of chloride of calcium. In experiments of this nature upon such a small quantity of the chloride considerable loss of lead must be expected. It is completely reduced when heated with black-flux. Chloride of lead suffers no reduction when heated to redness with common rosin or colophany. When chloride of lead is heated with an excess of sulphur in a close vessel, Berthier states that chloride of sulphur is evolved, and a grey sulpho-chloride of lead formed, the composition of which, it was supposed, might be nearly that indicated by the formula $PbS + 2PbCl$.[2] If so, the reaction would be expressed by the following equation :—

$$3PbCl + S^2 = PbS + 2PbCl + S^2Cl.$$

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[1] Gmelin's Handb. 5. p. 145. Berzelius, Tr. d. Chim. 4. p. 68. Handwörterb. der Chem. 1842, 1. p. 816, and Supplement, 1850, p. 563. [2] Tr. des Ess. 2. p. 685.

According to Berthier, chloride of lead and galena unite in any proportions by the *dry way*, yielding very fusible and volatile products which have a strong tendency to percolate through earthen crucibles. The product of the fusion of 1 equivalent of chloride with 1 of sulphide of lead exactly resembles galena; and that of the fusion of 4 equivalents of chloride with 1 of sulphide is compact, opaque, pale-grey of an olive hue, even and wax-like in fracture.

According to Berzelius a salt of the formula $PbCl+3PbS$ may be prepared by digesting recently precipitated sulphide of lead with a solution of chloride of lead in excess. It is yellow and sometimes red. The red colouration which occurs at first when a feeble current of sulphuretted hydrogen is passed into solutions containing lead and hydrochloric acid is due to the formation of this salt, which by further action of the gas is decomposed, the whole of the lead being changed into sulphide.

It is asserted on the authority of Göbel that at a red-heat chloride of lead is completely decomposed by carbonic oxide with the formation of phosgene gas and the separation of the lead in the metallic state,[3] thus:—

$$PbCl+2CO=Pb+CO^2,CCl.$$

Oxychlorides of Lead.

Salts of this nature of the following formulæ have been described:—

I.—3PbCl, PbO.	IV.—PbCl,3PbO.
II.— PbCl, PbO.	V.—PbCl,5PbO.
III.— PbCl,2PbO.	VI.—PbCl,6PbO.

No. II. is a white, insoluble powder and constitutes Pattinson's oxychloride.[4] It has been found native at Cromford, near Matlock, Derbyshire, and has consequently received the name of Matlockite. It may be obtained by the addition in proper proportion of lime-water to a hot aqueous solution of chloride of lead formed by heating strong hydrochloric acid with galena in fine powder. The same salt is stated to be produced by heating chloride of lead with free access of atmospheric air until fumes cease to be evolved; or it may be made by melting together chloride and protoxide or monocarbonate of lead. The oxychloride easily melts, and while molten is deep yellow; but when solidified is white and crystalline. At my request, my friend, Mr. Lowthian Bell, son-in-law of the late Mr. Pattinson, who carries on the manufacture of this pigment, has obligingly prepared for me a description of the process, which will be found at p. 81.

No. III. is found in nature and is known under the name of Mendipite, one of its localities being the Mendip Hills in Somerset-

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[3] Berzelius, Tr. de Chim. 4. p. 70.

[4] Patented April 3, 1839, No. 8020; Feb. 14, 1849, No. 12,479; and May 1, 1852, No. 14,104. See Chemical Gazette, 1849, 7. p. 366.

shire. By melting together chloride and protoxide of lead in the ratio PbCl : 2PbO I obtained a yellow product crystallized in needles.

No. IV. may be directly prepared by melting together at a bright red-heat chloride and protoxide of lead in the proportions indicated by its formula. In mass it is greenish-yellow and laminar, but its powder is pale yellow. It may be obtained in combination with 4 equivalents of water by the addition of caustic ammonia to a boiling aqueous solution of neutral chloride of lead, or by the admixture of a basic salt of lead with solutions of metallic chlorides.[5] This salt is particularly interesting from the fact that it is said to result from the action of moist litharge upon chloride of sodium, caustic soda being also formed. This discovery was made by Scheele, and it was hoped that it might furnish a solution of the then difficult problem of economically manufacturing soda from common salt. The two substances should be intimately mixed in the proportion of 1 part of salt to 4, but according to Vauquelin 7, of litharge, the mixture made into thin paste with water and left during several days; the mixture whitens, thickens, swells up very much, and becomes hard, so that from time to time it must be triturated with the addition of water. The solution got by washing the product with water and filtering, had a strong alkaline taste, and contained a little chloride of lead, but no chloride of sodium. By evaporation it yielded crystals of carbonate of soda, contaminated with chloride of lead. The washed insoluble residue when dry was dirty white, and by gentle heating became fine lemon-yellow. Curandeau found that the reaction was promoted by heat or by the addition of $\frac{1}{10}$th by weight of lime, and impeded by carbonic acid, and he recommended exclusion of atmospheric air. Red-lead gives a similar result to that obtained with litharge. Anthon states that when common salt is mixed even with 10 times its weight of litharge, left for 12 days and frequently stirred, it is only half decomposed. It is recorded that manufactories were established in England for carrying out this process.[6]

No. V. is produced by melting together chloride and protoxide of lead in the ratio PbCl : 5PbO. The product is orange-yellow and deep yellow when in powder. No. VI. is the pigment termed "Turner's Patent Yellow." It was the subject of a patent, and in the specification it is directed to be prepared as follows: "Take any quantity of minium, litharge, or calx of lead, add half the weight of common salt, with water sufficient to dissolve it; mix these by long trituration, and let them stand together at least for 24 hours, by which time the lead will be changed into a good white; then wash out the alkali and calcine the lead until it becomes yellow, which will be of different tints according to the continuance of calcination

[5] Berzelius, 4. p. 71.

[6] Vide Journ. des Mines, Vendémiaire de l'an III., No. 3, p. 44, in an interesting paper on the history of the decomposition of common salt. Thomson's System of Chemistry, 1804, 2nd ed. 2. p. 316. Aikin's Chemical Dictionary, 1807, 2. p. 27. Gmelin's Handb. 5. p. 147. Handwörterb. der Chem. 1842, 1. p. 817.

and degrees of heat."[7] This pigment is also described under the name of Cassel-yellow, and, according to Gmelin, is commonly made by melting a mixture of 1 part by weight of sal-ammoniac with about 10 parts of massicot, minium, or white-lead. Some of the sal-ammoniac is volatilized undecomposed, and part of the lead is reduced to the metallic state by the hydrogen of the ammonia. The product is fine yellow and crystallized in radiated laminæ.[8] By slow cooling it crystallizes in cubes. It is suggested that Turner's Patent Yellow is No. IV. and not No. VI. or Cassel-yellow.

According to Berthier, litharge partially decomposes chloride of sodium by the *dry way*, and melts easily with chloride of barium or calcium, producing yellow crystalline insoluble oxychloride resembling Turner's Patent Yellow, from which water separates the excess of chloride of barium or calcium mixed with baryta or lime respectively.[9]

Manufacture of Oxychloride of Lead.[1]

The value of the "white-lead" of commerce as a pigment, and the tedious character of its manufacture, early invited the attention of chemists, scientific as well as practical, in the hope of devising means for obtaining this well-known substance by a process more direct and shorter than that of exposing sheets of lead for many weeks to the action of vinegar and the carbonic acid evolved by the fermentation of spent tanner's bark. Attempts to convert litharge and metallic lead into carbonate by the direct action of carbonic acid were tried, and after immense outlay were all abandoned. The products obtained were either inferior to the article they were intended to supersede in point of colour, or they were deficient in "body," *i.e.* the power pre-eminently possessed by the old white-lead of covering, as paint, the surface to which it is applied. A considerable establishment was organized near Newcastle-on-Tyne by the late Dr. Richardson to produce a lead pigment in the form of the sulphate of that metal; but this, like all its predecessors, ended in failure.

The necessity which arose for the soda-makers on the Tyne condensing the large quantities of hydrochloric acid, given out in their rapidly increasing manufacture, placed in the hands of the inventor a new and valuable agent. The possibility of its being likely to prove serviceable in simplifying the method of making white-lead at once occurred to the mind of the late Hugh Lee Pattinson, the inventor of the ingenious and valuable process of desilverizing lead by crystallization. The fact that hydrochloric acid is capable of expelling the sulphur from *galena*, placed within his power the means of obtaining the metal in a state of combination ready for chemical treatment without being compelled in the first instance to have recourse to the smelting-furnace. Mr. Pattinson's first trials, like those of preceding experimenters, were directed to make carbonate of lead.

[7] Aikin's Chem. Dict. 2. p. 28.
[8] Gmelin's Handb. 5. p. 147.
[9] Tr. des Ess. 2. p. 685.

[1] Description by Mr. I. L. Bell, son-in-law of the late Mr. Pattinson.

The galena was finely ground, heated with hydrochloric acid at a low temperature, dissolved and crystallized. The crystals along with a little water and "whiting," which is a tolerably pure carbonate of lime, were ground together in a potter's flint-mill for some hours. Double decomposition ensued by which chloride of calcium and carbonate of lead were formed. The salt of lead thus obtained possessed however neither a sufficiently good colour nor body to induce Mr. Pattinson to persevere in attempting to overcome other difficulties connected with its manufacture.

His next efforts were to precipitate from a purified solution of the chloride of lead a carbonate by means of a bicarbonate of magnesia, which was procured by dissolving magnesia out of dolomite by means of carbonic acid evolved by the action of hydrochloric acid in carbonate of lime. No greater success attended the scheme than that of treating the crystals of chloride of lead with carbonate of lime; but Mr. Pattinson's researches in connection with the second process ended in the development of a greatly improved method of manufacturing magnesia, one which has since superseded the old plan of precipitating this earth from its salts by means of carbonate of soda. Never losing sight of the chloride of lead as the starting point of his operations, Mr. Pattinson threw down from a solution of this salt various compounds of oxide and chloride of lead, known as oxychlorides. These vary considerably in composition according to the conditions under which they are produced. He ascertained that one of these, viz., the neutral oxychloride (PbCl,PbO), could be, by careful treatment, produced of a fine white colour, and also, he believed, with a "body" at least equal, if not superior, to that of the old white-lead. After various modifications, the following is the process now carried on at the manufactory in the county of Durham by the Washington Chemical Company, the firm of which the late Mr. Pattinson was a partner and the founder.

The lead ore, galena, is ground along with hydrochloric acid in a machine resembling in all respects the potter's flint-mill, save that no part of it is of material readily attacked by the acid used in the operation. In from 30 to 40 hours the whole, or nearly the whole, of the galena and associated metals are converted into chlorides. A portion amounting to from 7% to 10%, however, remains either unacted on or converted into sulphate by the traces of sulphuric acid always found in the hydrochloric acid of the soda manufacturers. The following is an analysis of this portion of the lead ore after having been ground with the hydrochloric acid:—

Sulphate of lead	30·4	
Sulphide of lead	21·5	
Sulphide of zinc	7·2	
Sulphide of arsenic and antimony	1·8	
Quartz, &c.	19·7	
		80·6
To which must be added a quantity of chloride of lead not separated in the subsequent solution of the mass		19·4
		100·0

To these substances may be added all the silver found existing in the lead ore; at least this metal is rarely if ever found in the oxychloride of lead, and the residuum always shows a quantity equal to about 1 oz. to the ton of lead ore used beyond that indicated by assay, which corresponds pretty nearly with what might be expected from the nature of the mode of examining ores of lead previously to purchase.

The "rough chloride," as it is called, consists now essentially of two portions, the residuum above described and the chloride of lead which has to serve in the manufacture of the oxychloride. This chloride of lead, however, is accompanied by other chlorides, viz., those of iron and manganese, and other impurities which may exist either in the lead ore or in the hydrochloric acid. The presence of these salts in even very minute quantities would render valueless the oxychloride prepared from chloride of lead containing them. The greater portion is removed in the first instance by the free acid, which always accompanies the preparation of the rough chloride, and which is incapable of holding any lead in solution. The rough chloride is run from the grinding mill into a wooden vessel or "dolly," which is a large tub furnished with an agitator. The free acid is drawn off and cold water added, agitation being applied at the same time. This operation is continued until no iron reaction is perceived on the addition of the usual tests for this metal. This is usually effected in six or eight washings. The chloride being very sparingly soluble in cold water, little loss of lead arises from the treatment, and this little is avoided by returning the water of the last washings to the rough chloride as it is received in the dollies when the presence of free acid throws the chloride of lead down from the solution. The extreme solubility of the impurities sought to be removed by the washing of course greatly favours the operation just described. However, the amount of impurity capable of affecting the colour of the oxychloride is so extremely small that the washing process has occasionally to be supplemented by the addition of some chemical re-agent for removing the last traces of iron.

The "purified chloride" is now ready for solution, and to effect this two wooden tubs, about 12 feet deep and 9 feet in diameter, are placed side by side, and through them a stream of hot water flows uninterruptedly while the dissolving process is going on. These tubs or "dissolvers" are furnished with agitators which keep the liquid they contain in constant movement. Portions of the purified chloride of lead are let in from time to time, which are conducted by a pipe to the bottom of the first dissolver. The revolution of the mass prevents the chloride settling to the bottom, but not any larger particles of lead ore which may have escaped the action of the hydrochloric acid. This and the flow of hot water keep the solid mass suspended for a considerable time in the first dissolver, during which time the chloride of lead is being dissolved. It, along with the current of solution, then flows over into the second dissolver, to the bottom of which both are conveyed by a pipe as in the first instance. From this second vessel,

where the operation is completed, the solution flows into settlers in order to deposit the "residuum," the analysis of which has already been given. As something like 40,000 cubic feet of hot water is used in practice to dissolve one ton of chloride of lead, it is needless to remark that the presence of any sulphates or carbonates dissolved in even very small quantities would act very prejudicially in throwing down salts of lead which would then find their way into the residuum.

The substance used for precipitating the oxychloride of lead is lime, and for this object it is dissolved by allowing a stream of cold water to pass through vessels containing it. A perfectly clear solution is obtained by allowing the mixture to settle in large tanks or ponds enclosed in a building, to prevent the entire conversion of the lime into carbonate of lime by the action of the atmosphere. From two long orifices a stream of each of the solutions obtained in the manner just described is permitted to flow in such proportions as to indicate by chemical tests a slight excess of lead. This precaution is observed for the following reasons: first, it was discovered that an oxychloride containing a very small excess of oxide had photogenic properties, and was in consequence liable to change on exposure to light to a yellow colour, a very objectionable tint for white-lead; and, secondly, the oxychloride itself was probably from its great affinity for oil liable to harden in the casks containing it on keeping. This led to the introduction of a small quantity of carbonate of lead during the process of manufacture, the presence of which was found to obviate the inconvenience frequently otherwise complained of. The carbonate of lead necessary for the purpose is formed by adding a small quantity of a soluble carbonate such as that of soda. The current of water flows through a series of tanks which intercept the oxychloride of lead just precipitated, the excess of water is filtered off and the precipitate placed in earthen dishes in stoves in the manner followed in drying white-lead made in the ordinary way. The oxychloride thus obtained is of a fine silky texture and of a beautiful white colour, occasionally with a faint shade of blueness in the crevices of a large mass. Its specific gravity is stated to be 7·04, while that of white-lead is 6·67. In grinding it with oil for paint the operation is conducted precisely in the method pursued in the old white-lead works. [It requires, however, I am informed, a considerably larger proportion of linseed-oil than is employed for ordinary white-lead, and much more oil of turpentine for the painter's use.—J. P.]

Chlorocarbonate of Lead.

$PbCl + PbO,CO^2$.—It may be prepared by boiling with water chloride and monocarbonate of lead in the ratio of the formula. It is a white, heavy, insoluble powder, which melts easily, and on increasing the temperature loses its carbonic acid, being converted into oxychloride. It has been found native at Tarnowitz in Upper Silesia.[2]

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[2] Rammelsberg's Handb. der Mineralchem. 1860, p. 245.

LEAD AND NITROGEN.

Nitride of Lead.

No compound of lead and nitrogen has yet been described.

Nitrates of Lead.

Neutral or mononitrate. PbO,NO^5.—It may be prepared by the action of nitric acid upon lead, when nitric oxide (NO^2) is disengaged; or by digesting protoxide of lead in warm dilute nitric acid. It crystallizes in the cubical system, and the crystals usually deposited on the cooling of hot solutions, are opaque, white, and lustrous; whereas, it is stated that by spontaneous evaporation from a cold solution they are obtained transparent. It is very soluble in water: at 10° C. 1 part by weight dissolves in 2·07 of water, and at 100° C. in 0·72. It is less soluble in water acidulated with nitric acid, so that it is partially precipitated by the addition of this acid to its saturated aqueous solution. It is insoluble in concentrated nitric acid. It is permanent in the air. When heated to redness it decrepitates and melts; fumes of hyponitric acid and oxygen are given off and protoxide of lead is left, as shown by the equation[1]

$$PbO,NO^5 = PbO + NO^4 + O.$$

Paper steeped in a dilute solution of this salt and dried is "touch-paper," that is, it continues to burn after ignition like tinder. Nitrate of lead when heated is a highly oxidizing substance.

Basic nitrates of protoxide of lead.—Not fewer than four basic nitrates of protoxide of lead have been described. One only, the bibasic nitrate, may be adduced in illustration, of which the formula is

$$2PbO,NO^5, \text{ or } 2PbO,NO^5,HO.$$

It may be made by boiling an aqueous solution of neutral nitrate with the fine powder of protoxide of lead in the ratio of equivalent to equivalent; or white-lead may be substituted for protoxide, when carbonic acid will escape with effervescence; and it may be used in excess, for as soon as the neutral has been converted into bibasic nitrate no further action takes place. This salt is precipitated as white powder when caustic ammonia is added to an aqueous solution of neutral nitrate, the latter being in excess. It is sparingly soluble in cold and much more soluble in boiling water. During evaporation by artificial heat it is deposited in fine scales; but by slow evaporation it is separated in small opaque crystalline grains, which, according to Berzelius, decrepitate with extraordinary violence when heated, notwithstanding they contain no water of combination.[2]

Hyponitrates and nitrites of protoxide of lead. — For information

[1] Berzelius, Tr. de Chim. 4. p. 82. Handwörterb. der Chem. 1859, 7, p. 151. Gmelin's Handb. 5. p. 158.

[2] Tr. de Chim. 4. p. 83.

concerning these salts chemical treatises must be consulted. A short description, however, chiefly by Berzelius, of certain nitrites will here be appropriate.[3] When a solution of 1 part by weight of neutral nitrate of lead (PbO,NO^5) in 50 of water is boiled with $1\frac{1}{2}$ of pieces of lead in thin sheet so long as lead dissolves, a salt of the formula $4PbO,NO^3$ is deposited on cooling in little brick-red coloured scales, which are often aggregated in hemispherical clusters. If the solution is too concentrated, the salt is deposited upon the lead during the process of preparation, and its colour is in that case pale, though its composition be the same. It dissolves with great difficulty in cold water, has a strong alkaline reaction, and is permanent in the air. After calcination protoxide of lead is left as the product. By passing carbonic acid through the hot aqueous solution of this salt carbonate of lead is precipitated, and the supernatant liquor, which is yellow, lets fall spontaneously or by evaporation *in vacuo* long yellow prisms or yellow plates of neutral nitrite, *i.e.* of the formula PbO,NO^3+HO or $2HO$, chemists differing as to the proportion of water. This salt very easily dissolves in water and is easily decomposable.[4]

There are double salts of nitrate and nitrite of protoxide of lead.

LEAD AND ANTIMONY.

These metals readily unite when melted together, forming perfectly homogeneous alloys, which will be hereafter described under the head of type-metal in the article on the Metallurgy of Tin. It is only necessary in this place to treat of certain oxidized compounds of the two metals, because a knowledge of these is essential to the right understanding of some important metallurgical operations connected with lead.

Antimoniate of Protoxide of Lead.

PbO,SbO^5.—It is thrown down as a curdy, white substance when an aqueous solution of antimoniate of potash is added to an aqueous solution of nitrate of protoxide of lead. It is also produced by digesting an alloy of lead and antimony in hot nitric acid; though when pure antimony is similarly acted upon by that acid it is only changed into oxide of the formula SbO^3. Prepared by either of these methods it is white and hydrated; but when heated moderately it becomes anhydrous and acquires a pale buff colour; but while hot it is sulphur-yellow. After having been heated to a higher degree it is brownish-red. It melts at a low white-heat, but, contrary to what has been stated, not without decomposition, as the following experiment made by R. Smith, in my laboratory, will demonstrate:—14·457 grains of the anhydrous antimoniate were heated to low whiteness in a shallow platinum vessel, in a muffle, during 5 minutes, when the loss amounted to 1·99 grains, *i.e.* 13·76%. The product was compact, hard, and brownish-red. It is not completely decomposed by acids,

[3] Berzelius, Tr. de Chim. 4. p. 85.

[4] Handwörterb. der Chem. 7. p. 190.

even when freshly precipitated. It is easily deoxidized by heating with charcoal. In its anhydrous state it forms the well-known pigment Naples Yellow, which came from Naples under the name of "Giallolino," and was for a long time regarded as a natural product.[1] Brunner has published the following receipt for its preparation:—An intimate mixture of 1 part by weight of tartar-emetic, 2 of nitrate of protoxide of lead, and 4 of common salt is gently heated during 2 hours in a Hessian crucible until the mass melts. After cooling, the product drops out when the crucible is inverted and tapped on the outside. The top of the cake consists of a layer of common salt, which is added with the object of preventing the reducing action of the carbon of the tartaric acid from being too violent. The cake is triturated and washed with water in order to remove the common salt. If the temperature at which fusion takes place is too high, the mass cannot be properly disintegrated, and the pigment will be of inferior quality. If the temperature does not exceed the melting-point of common salt, the tint inclines to orange; but beyond that degree it is lemon or sulphur-yellow. It is needful to urge that the ingredients employed should be as pure as practicable.[2] We have followed Brunner's directions with fair success. But it should be remembered that in the manufacture of pigments very slight, and what to the novice might be considered unimportant, conditions may have not only a decided but an extraordinary effect in modifying tint. On this account it is that disappointment has been so often experienced by persons in attempting to produce artists' colours from the meagre and not seldom erroneous directions given in what are received as standard works on chemistry. In this department of manufacturing art, as indeed, in every other, practical knowledge of value can only be acquired by experience, and even then, it may be, not until after many failures. Artists in using Naples Yellow are careful not to rub it on the palette with a steel knife, as it would be thereby blackened, notwithstanding it is ground up with linseed-oil.

When lead alloyed with antimony is calcined, say at a moderate red-heat, with free access of atmospheric air, both metals are quickly oxidized, but the antimony in greater proportion than the lead, antimoniate of protoxide of lead being formed. Hence, by means of calcination, lead may be practically freed from antimony; and, accordingly, such a process is adopted on the large scale in what is termed "softening," as will in the sequel be fully explained. By calcination of lead rich in antimony a serviceable yellow antimoniate of protoxide of lead may be made, and a patent for the manufacture of such a pigment has been granted to Mr. Dick.[3] The process is described as follows in the specification:—The dross formed in the process of softening lead by heating the metal with free access of air in a reverberatory furnace, and which consists essentially of oxides of lead, antimony, and arsenic, is calcined in a reverberatory

[1] Tschelnitz, Farben-Chemie, 1857, p. 42. Lefort, Chimie des Couleurs, 1855, p. 105.
[2] Berzelius, Tr. de Chim. 4. p. 108. [3] A.D. 1858. No. 2561.

furnace. Calcination is at first conducted at a low heat or a heat below redness, and afterwards at redness during the remainder of the process. The duration of the calcination depends upon the quantity of dross operated upon. In practice, it has been found that calcination during three days suffices for 30 cwts. of dross. During the latter part of the process it has been found desirable that a quantity of common salt (NaCl) should be added to, and mixed with the dross. Salt in a proportion not exceeding half the weight of the dross answers well in practice. The calcined product may be saturated with sulphuric, hydrochloric, or acetic acid, or it may be exposed to the vapour of acetic acid in stacks of bark, after the manner practised in the manufacture of white-lead. But this part of the treatment is not insisted upon, as a yellow pigment may be produced by simply heating the dross in contact with air. The quality, however, of the pigment is improved by the use of common salt, or of the acids above specified. After the full effect of the heat has been produced, and the quality of the pigment is not improved by further calcination, the dross is removed from the furnace washed and ground, when its manufacture is complete. Brunner states that a cheap but inferior quality of Naples Yellow is produced by heating to redness 1 part by weight of the powder of an alloy consisting of equal weights of lead and antimony in admixture with 3 of nitre and 6 of common salt, and afterwards grinding and washing the product as in the method previously described.[4]

Naples Yellow is used as an enamel colour. In 1852 I examined a piece of enamelled brick from the Kasr ruins of Babylon. The enamel had a yellow colour much resembling that of solid gamboge; it was streaked or mottled throughout with a yellow substance like orpiment in tint; it was more or less porous or cellular; its surface was here and there coated with an iridescent film; it was about $\frac{1}{16}$ inch thick, and had run down irregularly over the sides in drops of greater thickness. I extracted from it lead and antimony, and therefore inferred that the yellow colour was due to antimoniate of protoxide of lead.

ALLOYS OF LEAD.

Lead and Potassium.

Gay-Lussac and Thénard prepared an alloy of these metals by heating two measures of potassium covered with eight measures of fine lead-filings. The apparatus used for this purpose was a glass tube closed at one end and drawn out at the other, but not sealed. The alloy was formed as soon as the lead melted. It is described as solid, very fusible, very brittle, and very fine-grained in fracture. Reduced to powder, it is gradually decomposed in the air; it effervesces vigorously in water, and more so in acids; in all these cases the potassium is oxidized and separated as potash, while malleable lead

[4] Gmelin's Handb. 5. p. 175.

remains.[1] Vauquelin states that by heating oxide of lead with cream of tartar, a button of lead is obtained, which is grey and fibrous in structure; that a freshly-cut surface of this lead tastes strongly alkaline; that when a piece of moist red litmus-paper is laid upon such a surface, it instantly becomes blue; but that no hydrogen is evolved by the action of water on this lead.[2] According to Serullas, by heating an intimate mixture of 100 grammes of protoxide of lead and 60 of carbonized cream of tartar, an alloy of lead and potassium is formed, which is silver-white and very brittle. By the addition of 5 or 6 grammes of lamp-black to the mixture, the product is rendered pyrophoric. Several experiments are recorded on alloys of lead and potassium prepared in a similar manner.[3]

When cream of tartar (bitartrate of potash) is strongly heated, oxide of potassium is reduced by the carbon resulting from the carbonization of the tartaric acid, and potassium is volatilized; so that the production of lead alloyed with potassium might have been reasonably anticipated under the conditions above specified, provided the temperature should not be so high or so long maintained as to cause the volatilization of the potassium, which might have become alloyed with the lead.

The alkaline reaction of a freshly-cut surface of the alloyed lead prepared by Vauquelin is fallacious as an indication of the presence of potassium; for I find that on laying a piece of moistened red litmus-paper on a freshly-cut surface of the purest as well as of common commercial lead, it becomes rapidly blue.

The following experiments have been made in my laboratory. An intimate mixture of 1000 grains of red-lead and 300 of carbonized argol (impure cream of tartar of commerce) was strongly heated in an earthen crucible; and as most of the reduced lead was observed to be dispersed in small globules through the carbonaceous residue, the contents of the crucible were stirred with a stick in order to cause the lead to collect at the bottom, after which treatment the lead was poured into an ingot-mould. The ingot resembled ordinary lead, and was found to contain 0·523% of potassium. (J. C. Cloud.)

An intimate mixture of 2000 grains of finely-granulated lead and 300 of bitartrate of potash was covered with a layer of 100 grains of the same salt, and exposed in a covered and luted plumbago crucible to a high temperature during an hour; and the crucible was left to cool gradually in the furnace until the next day. There was a single button of lead in the crucible, which weighed 1910 grains, and the interior of the crucible and cover was lined with small globules of lead. There were only a few small buttons of slag, so that a very large proportion of the potassium present must have been reduced and volatilized. (R. Smith.)

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[1] Recherches Physico-Chimiques, 1811, 1. p. 218.
[2] Ann. de Chim. et de Phys. 1817, 7. p. 34.
[3] Ibid. 1822, 21, p. 200.

Lead and Sodium.

The two following alloys of these metals were made and described by Gay-Lussac and Thénard; and the process which they followed was the same as that detailed in the preceding article on Lead and Potassium.[4]

I. The proportions taken were one measure of sodium and four measures of fine lead-filings. The alloy was formed, without emission of light, as soon as the lead melted. It is described as somewhat malleable, blueish-grey, very fine-grained in fracture, sensibly caustic to the tongue, and nearly as fusible as lead. It is slowly decomposed in the air, and does not cause lively effervescence with water, but does so with acids. In every case, the sodium is gradually changed into soda, and separated from the lead.

II. The proportions taken were one measure of sodium and three measures of fine lead-filings. The alloy was formed, without emission of light, as soon as the lead melted. It is described as brittle, blueish-grey, fine-grained in fracture, and caustic to the tongue. It resists the action of the air less than the preceding alloy, effervesces pretty strongly with water, and more so with acids. In every case, the sodium is gradually converted into soda and separated from the lead.

The following experiments have been made in my laboratory. Sodium, with a cleaned surface, weighing 24 grains, was wrapped up in 104 grains of lead-foil, and was carefully heated in a test-tube until fusion occurred. The product was solid, blueish-grey, very brittle, largely crystalline, but seemingly not perfectly homogeneous in fracture. A freshly-cut surface became tarnished immediately in the air. Great effervescence took place when water was poured on the powder of the alloy, and after a time a spongy mass of lead remained. When the alloy was put in pieces of considerable size into water, copious evolution of hydrogen followed, and lead was left in a granular form. (C. Tookey.)

Lead was melted under charcoal in an iron ladle, sodium was dropped in, and the contents stirred well with a stick of wood, when much scum was formed. The metal was poured into an iron ingot-mould. The ingot resembled ordinary lead in appearance; but the freshly-cut surface tarnished rapidly in the air, passing through various shades of yellow, brown, and blueish-black, to nearly black at last. The alloy contained only 0·394% of sodium. The alloy produced in another similar experiment contained 0·295% of sodium. (J. C. Cloud.)

It may be predicted with confidence that if, as has been stated, lead may be alloyed with potassium by heating a mixture of oxide of lead and carbonized cream of tartar, it may also be alloyed with sodium in a similar manner. An alloy of lead and sodium is said to be produced when lead is heated with charred soap.[5]

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[4] Recherches Physico-Chimiques, 1811, 1. p. 241.
[5] Gmelin's Handbook of Chem. 5. p. 162.

Lead and Copper.

When lead and copper are melted together at or beyond the fusing point of copper, and the molten metal, after having been well stirred, is poured into an ingot-mould and very quickly cooled, an apparently homogeneous product or alloy is obtained. In the proportion by weight of 3 parts of lead to 1 of copper, the product is brittle; the fracture is granular and lead-grey, and the external surface has a coppery tinge. If this alloy, or any other composed of lead and copper in relatively large proportions, similarly prepared, is kept heated for a considerable time at or somewhat beyond the melting-point of lead, liquation will occur; lead containing copper will trickle down, and a more or less porous mass of copper containing lead will eventually be left. A similar result will take place if the molten mixture of these metals is very slowly solidified. According to Karsten, on subjecting an alloy, consisting of lead and copper in about the proportion by weight of 3 to 1, to the most careful liquation possible, the separated lead contains from 2% to 2·8% of copper; and the copper retains about 25% of lead.[6] Assuming the metal from which lead has thus been drained to consist of solid copper infiltrated with molten lead, it is clear that a considerable quantity of lead must be retained by the copper, which could only be squeezed out by external pressure, or by powerful cohesive attraction amongst the particles of copper.

It has been maintained that the so-called alloys of lead and copper are only mixtures of the two metals; but this is a question which it would be useless to discuss in the absence of a precise and accepted definition of the word alloy. If mixtures of metals obtained by fusion be excluded from the definition, it would follow that alloys must be chemical compounds, or the products of the solution of one metal in another, or both. The subject will be elsewhere duly considered. It is certain that when lead is brought into contact with molten copper, it will take up some of this metal, and retain a small portion of it even after having been subjected to most careful liquation, whether by slow cooling after fusion or gradual re-heating after solidification; and the copper so retained will be found uniformly diffused through the lead. The case is precisely analogous to what occurs when lead and zinc are melted together, and slowly solidified; the metals separate from each other, but the lead retains a little zinc, and the zinc a little lead. (See the first volume of this work, article Zinc.)

The following statements concerning the liquation of cupriferous lead are given on the authority of Reich.[7] When cupriferous lead is melted at the lowest possible temperature, and the unmelted or half-melted substance, termed *Abzug*, swimming on the surface, is removed, this *Abzug* will contain most copper, and the residual lead will be

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[6] Karsten, System der Metallurgie. 1832, 5. p. 441.

[7] Jahrbuch für den Berg- und Hüttenmann, Freiberg, 1860, p. 186.

proportionately poor in copper. But when the temperature is raised and the *Abzug* is not removed, the proportion of copper in the lead rapidly increases with the temperature. "Unrefined soft lead" was melted in a refining furnace by slowly raising the temperature, and after the lapse of two hours, when it had scarcely reached incipient redness, the *Abzug* was taken off. The subjacent lead contained 0·08% of copper, while the *Abzug*, which was wholly in the metallic state and rich in lead, contained 5% of copper. This *Abzug* was melted in a porcelain crucible, for which nearly a red-heat was required; and on the surface appeared a pulverulent and partially oxidized mass, which contained 20% of copper, while the subjacent lead contained only 0·4%. Lead containing 0·974% of copper was melted at a moderate heat in a porcelain crucible, and yielded unmelted *Abzug*, which contained 14·84% of copper. From the preceding results it will be seen, that in liquating cupriferous lead in the manner described, the proportion of copper in the lead separated is greatly influenced by temperature.

When an alloy or mixture, consisting of lead and copper in large proportions, is exposed during a long time to the action of the atmosphere at ordinary temperatures, it becomes oxidized to a considerable depth. The following observations on this subject by myself are, I think, worth recording. In July, 1846, copper containing 2·2% of silver was melted with three times its weight of commercial soft lead, and the molten mixture was poured into a flat closed iron ingot-mould of the usual construction. On the 2nd of December, 1869, the ingot, which had been preserved in a cabinet, was examined. It was nearly $\frac{5}{16}''$ thick, $5\frac{3}{4}''$ long, and 2″ broad at the bottom, but a little narrower toward the top, where it had seemingly contracted somewhat during solidification. Its surface was rough, and coated thinly with dull blueish-grey matter, which under a lens appeared finely granular and more or less cellular. Below a line, which will be designated by the letter L, extending round the ingot at about $2\frac{1}{4}''$ from the top, were numerous low, circular, crater-like prominences. On both sides above L, and along a broad central band extending below L to the bottom, after scraping off the superficial grey coating, the encrusting substance underneath was found to be about $\frac{1}{16}''$ thick, hard, tenaciously adherent, yellowish-brown, and dull, but when cut, shining and more or less metallic in lustre. On bending an upper and lower corner of the ingot, portions of this crust were detached in flakes, and the surface thereby disclosed differed in appearance from that produced by scraping: it was chocolate-brown, and singularly pitted, as though it had been formed by the aggregation of flattened circular masses about $\frac{1}{4}''$ in diameter. Within the crust was a layer apparently of unchanged alloy about $\frac{1}{3}$ of the thickness of the ingot. The powder obtained by triturating the crust was light yellowish snuff-brown. On cutting the surface of the rest of the ingot, which was free from this crust, the metal resembled lead.

On boiling the brown crust with aqueous solution of potash, insoluble matter was left, which, when magnified from 50 to 100

diameter, was found to consist of bright crystals, apparently of metallic copper, many of which were aggregated in star-like clusters.

The brown crust and superficial coating have been analysed by Mr. Ward, in my laboratory, and found to have the following composition per cent. :—

ANALYSIS OF THE BROWN CRUST.

Lead	81·59
Copper	9·48
Silver	0·78
Oxygen	6·28
Carbonic acid	1·47
Water	0·32
	99·92

The quantity of oxygen found by passing hydrogen over the crust at a red-heat was 6·28%, exclusive of what was ascertained to exist in the state of water; and the quantity found by calculation, on the assumption that the lead was present in the state of protoxide, is 6·299%. The carbonic acid is doubtless in combination with protoxide of lead. From these data it may be inferred that the ingot was originally not homogeneous, and that the lead had been oxidized, while the copper had remained in the metallic state. The crystallization of the copper, under the circumstances, is an interesting fact; and it is probable that it occurred during the solidification of the ingot. I may mention a seemingly analogous fact which I observed in an ingot obtained by melting a mixture of copper and metallic tungsten. The tungsten, it may be shown, is for the most part mechanically diffused in such an ingot; for when a portion of the latter is digested in dilute nitric acid, the tungsten is left in the state of crystalline powder.

The superficial coating contained 78·06% of protoxide of lead and 14·40% of protoxide of copper.

LEAD AND MANGANESE.

Berthier tried to obtain an alloy of these metals by heating mixtures of protoxide of manganese, litharge, and charcoal in a brasqued crucible to a high temperature (150° Wedgwood's pyrometer). He records the results of two experiments, of which one was unsatisfactory from a deficiency, he supposed, of charcoal. In the other experiment the oxides were mixed in the ratio of equivalent to equivalent, and the quantities operated upon were as follow:—

Protoxide of manganese ...	8·92 grammes	=	metallic manganese ...	6·91
Litharge	27·89 id.	=	metallic lead.....	25·89

A button, weighing 34·7 grammes was obtained, which is described as homogeneous, compact, and very ductile; it was rolled into very thin leaves, having much lustre, which broke on attempting to fold them, and of which the fracture was granular and very dark-grey. Now, the sum of the weights of metallic manganese and metallic lead in the mixture treated is 32·80 grammes; but the weight of button produced is 34·7 grammes. Yet Berthier states that much

lead was volatilized during the experiment. This increase in weight might be partly accounted for by carburization of the manganese. Supposing no loss to have occurred, and reduction of both oxides to have been complete, the button should have consisted of 21·0% of manganese, and 78·9% of lead. In small experiments of this kind, merely mechanical mixtures are apt to be mistaken for combinations. Lead mixed with a large proportion of finely-divided and mechanically diffused foreign matter, might be rolled into comparatively thin sheet. It will require more satisfactory evidence than the foregoing to establish even the possibility of alloying lead with manganese.

Experiments on this subject have been made in my laboratory by Hochstätter. Carbonate of manganese and protoxide of lead were mixed in the ratio of equivalent to equivalent, and strongly heated in brasqued crucibles. Much loss occurred from volatilization of lead, and the products seemed to be merely mechanical mixtures of lead and carburized manganese. When breathed upon the smell of fetid hydrogen was perceived.

ORES OF LEAD.

Sulphide of lead. Galena. Blue-lead. Galenit, Bleiglanz (German), Galène (French). PbS.—When pure (Pb = 103·46) it contains 86·61% of lead and 13·39% of sulphur. It may be regarded as *the ore* of lead, the total quantity of the other ores of lead being comparatively insignificant. The word galena does not occur in Greek,[1] and its derivation is unknown. It was certainly used by Pliny in the sense of lead ore, who has given the following definition of it:—Est et molybdæna quam alio loco galenam appellavimus, vena argenti plumbique communis.[2] (Molybdæna, which we have in another place called galena, is equally the ore of silver and of lead.) Galena is widely, though not abundantly, distributed over the earth.[3]

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[1] The Greek word for lead is, μόλιβδος or μόλυβδος. Μολίβδαινα or μολύβδαινα is a mass of lead.

[2] Naturalis Historia, Sillig's edition. Lib. xxxiv. Cap. xviii. Sect. 53. See Beckmann's History of Inventions, English transl. by Johnston. London, 1814. 4. p. 11. Also Zippe's Geschichte der Metalle, 1857, p. 191. According to Zippe the Greek word μόλιβδος is derived from the Sanscrit Mulva, and hence he infers that the knowledge of lead came to the Greeks from the East. Beckmann justly remarks that the notion of galena having been derived from γελέω, to shine, is negatived by the fact that the word galena is not found in the works of Greek authors.

[3] I have received from my friend, Mr. Bauerman, the following note concerning alquifoux, which has considerable interest:—"The word *alquifoux*, used in France and Germany to distinguish the large and coarse-grained lumps of galena which are sold for pottery purposes, also known as potters' ore or Glasurerz, is derived from the Italian *archifoglio*, literally large-leaved, which is the name applied to this kind of lead ore in the Levant trade, it being exported in considerable quantity to Egypt to be employed as a remedy in ophthalmia, as well as for painting the eyelids. The Arab name is Kohlhe. It is generally supposed that sulphide of antimony was used for the latter purpose, but, according to Dr. Figari Bey, this is not the case. I have heard that some years ago an enterprising Arab fetched several camel-loads of *pyrolusite* out of the desert, which gave a soft powder of good strong colouring power, and was sold for the same purpose, but the experiment does not appear to have been successful, as it has not been repeated. The following extract is from Dr. Figari Bey's list of Arab drugs: 'Studii scientifici sull' Egitto,' vol. ii. p.

Galena crystallizes in the cubical system. It cleaves easily into cubical fragments. Its hardness is 2·5, *i.e.* midway in that respect between rock-salt and calc-spar. It varies in structure from largely crystalline to finely granular, or, as it is termed, steel-grained. I have a specimen found in carboniferous coal at Bedworth in Warwickshire, which is in the form of a more or less spherical apparently concretionary mass.

In Great Britain galena occurs in veins in palæozoic rocks, namely, in the Carboniferous or Mountain Limestone in Cumberland, Durham, Northumberland, Yorkshire, Derbyshire, and Flintshire; in the Devonian in Devon and Cornwall; and in the Lower Silurian in Shropshire.

Various metallic substances may either be invisibly present in galena and then only in small quantity, or visibly associated with it. Amongst the former may be specially mentioned silver, gold, antimony, copper, iron, and zinc; and amongst the latter blende, iron-pyrites, magnetic iron-pyrites, mispickel, copper-pyrites, fahlore, brown-iron-ore, carbonate of iron, calamine, arsenical cobalt,[4] quartz, chalcedony, calcite, aragonite, pearl-spar (dolomite), strontianite, barytes (sulphate of baryta, called cawk in Derbyshire), fluor-spar, and actynolite (Strahlstein).

Manganese is stated to have been found by Sandmann in galena from the vicinity of Gladenbach, in Upper Hessen, which consisted of an aggregation of very small cubes, and had the specific gravity of 7·11: the following analyses of it have been published:—[5]

Sulphur	13·70	.....	13·90
Lead	83·45	.....	83·58
Iron	0·83	.....	0·83
Manganese	1·13	.....	1·26
Silver	0·14	.....	0·14
	99·25		99·71

Anthracite impregnated with galena occurs near Laak, in Carniola; and with it are also associated quartz, iron-pyrites, and traces of malachite and covelline (CuS). Pieces of anthracite, in which even with the aid of a lens no foreign matter could be perceived, contained 37·1% of sulphide of lead, 2·2% of sulphur soluble in bisulphide of carbon, and 0·008% of silver.[6]

It is a remarkable fact that silver should invariably be present in galena, sometimes, indeed, in very minute proportion; and the same generalization may now be received as established with respect

392—'Solfuro di *piombi* nativo (kohlhe) archifoglio in grandi lamine è adopterato in pulvero finissima come collirio secco.'" In describing the nature of the lead ores of the Sierra de Gador, in the South of Spain, Petitgand remarks that the massive ore, freed from gangue, or *alquifoux*, which is sold in its natural state for potteries, is termed *alcohol* or *alcohol de hoya*. (Exploitation et traitement des plombs dans le midi de l'Espagne. Revue Universelle, 1861, 9. p. 317.)

[4] I have seen minute quantities of this mineral, together with arseniate of cobalt occurring with galena, from the deepest part of the Snailbeach mine in Shropshire.

[5] Liebig and Kopp's Jahresbericht for 1854, published 1855, p. 809.

[6] Berg- und hüttenm. Jahrbuch, 1864, 13. p. 28.

to the presence of gold. In 1853 specimens of lead from different localities, some far distant from each other, of litharge, of red-lead, of white-lead, of Pattinson's oxychloride of lead, and of sugar of lead, were examined by my assistant, Mr. R. Smith, and myself, and in every instance we were able to extract a distinctly visible, though unweighable, quantity of gold, in addition to silver. Since then the substance deposited from lead-smoke has also been examined, and with the like result. The process employed was such as to render it impossible that error should arise from the introduction of the metals in the course of manipulation. The lead or compounds of lead operated upon were from Nenthead in Cumberland, from Snailbeach in Shropshire, from Derbyshire, from Bleiberg in Carinthia, from Przibram in Bohemia, from Tuscany, and in many other cases the localities were unknown.[7] Further evidence on this subject will be found in the table at p. 97.

What is the meaning of this constant association of silver and gold with galena? That is a question which eminently deserves the attention of students of chemical geology. It may be safely concluded that galena has for the most part been deposited through the agency of liquid water. It is known that it may be so deposited, as it has been found in the centre of nodules of clay iron-stone from the coal measures, which are certainly of sedimentary origin, and even in coal itself; and the examination of lodes containing galena, especially with regard to certain frequently attendant minerals and the mode of their association with it—minerals which have clearly been deposited from solution in water—leads to the same conclusion. During several years past nickel and cobalt have been carefully sought for in the numerous analyses of iron which have been made in the metallurgical laboratory under my charge, and in every instance either one or both have been detected, and in not a few cases in weighable quantities It may be that some great and important truth will one day be evolved from investigations of this nature.

The silver, it is certain, usually exists in galena in the state of sulphide, and so probably does the gold. It is rare to find gold visibly present in galena. I have received from the late Professor Nordenskiöld a specimen of galena containing a considerable quantity of gold diffused through it in particles: it is associated with quartz, and its locality is Beresowsk in Siberia.

The mode of existence of sulphide of silver in galena is not always the same, as may be inferred from the fact, that, by *washing*, nearly the whole of the silver is carried away from some kinds of galena; while by the *same treatment* of other kinds of galena the loss of silver is inconsiderable.[8] Great loss of silver by washing would seem to indi-

[7] A record of the experiments, except that relating to fume, was published in the Philosophical Magazine, 4 ser. 1854, 7. p. 126.

[8] See a Lecture on the Metallurgy of Lead, by Mr. J. A. Phillips, read before the Society of Arts, April 27, 1859. Alluding to specimens upon the table, Mr. Phillips remarked that "in the case of one of them the silver was almost entirely lost if the ore was treated by washing, whilst in the other the loss of silver, by similar treatment, did not amount to more than two ounces to the ton."

cate that sulphide of silver, or a compound of that sulphide and sulphide of lead, is mechanically diffused through a large mass of galena regularly or irregularly. In this case, owing to the specific gravity of sulphide of silver being lower than that of sulphide of lead, it is easy to understand how in the operation of *washing* there should be notable loss of silver.

It is an error to suppose that largely crystalline galena is generally poor in silver, and the proof that it is not so will be found in the accompanying table of results obtained by Mr. R. Smith, in the Metallurgical Laboratory of the School of Mines; and from this table it will also be seen that fine-grained galena is not always rich in silver.

TABLE SHOWING THE PROPORTION OF SILVER AND THE PRESENCE OF GOLD IN GALENA FROM VARIOUS LOCALITIES.

Locality.	Structure of the Galena.	Lead per cent. by dry assay.	Silver per cent. by dry assay.	Silver per ton of ore by dry assay.	Gold (500 grs. of ore operated upon).
				oz. dwts. grs.	
England— Yorkshire (Wensleydale)	Coarse-grained	80·5	0·0030	0 19 14	Traces.
Northumberland (Alston Moor)	Coarse-grained	80·0	0·0142	4 12 18	Traces.
Durham (Weardale)	Dressed ore	83·6	0·0120	3 18 10	Distinct traces.
Derbyshire (Alport)	Coarse-grained	82·0	0·0040	1 6 3	Traces.
Somersetshire	Large-grained	69·8	0·0410	13 7 21	Distinct traces.
Shropshire (Snailbeach Mine)	Large-grained (Potter's ore)	85·3	0·0016	0 10 11	Very minute trace.
Devonshire (Teign Valley)	Large-grained	79·2	0·0146	4 15 9	Very minute trace.
Leicestershire (Charnwood Forest)	Large-grained	81·0	0·0050	1 12 16	Very minute trace.
Cornwall	Large-grained	77·3	0·0640	20 18 3	Minute trace.
Cornwall	Large-grained	79·0	0·0316	10 6 11	Minute trace.
Isle of Man	Dressed ore	78·3	0·1470	48 0 10	Very minute trace.
Isle of Man	Dressed ore	79·4	0·1484	48 9 13	Very minute trace.
Spain	Very fine close-grained	84·2	0·0230	7 10 16	Minute trace.
Portugal	Large-grained	83·4	0·0120	3 18 10	Very minute trace.
Portugal	Coarse-grained	55·0	0·2480	81 0 6	Distinct traces.
France	Large-grained	80·2	0·3458	112 19 5	Distinct traces.
France	Large-grained	80·5	0·3348	109 7 8	Distinct traces.
France (Brittany)	Coarse-grained	77·0	0·1588	51 17 11	Distinct traces.
Sardinia	Fine-grained, containing crystals of anglesite	83·8	0·0106	3 9 6	Distinct traces.
Sardinia	Fine-grained	79·2	0·0054	1 15 7	Distinct traces.
Sardinia	Fine-grained and somewhat laminated	76·5	0·0228	7 8 23	Traces.
Switzerland		58·6	0·1500	49 0 0	Distinct traces.
Sweden (Sala)	Large-grained	75·2	0·7690	251 4 0	Distinct traces.
Greenland	Large-grained	82·5	0·1800	58 16 0	Distinct traces.
East Main Coast, Hudson's Bay (Whale River)	Very large re splendent cubes	83·8	0·0164	5 7 4	Distinct traces.
W. Indies (St. Kitt's)	Large-grained	83·9	0·0055	1 16 0	Very minute trace.
Turkey	Coarse-grained	61·3	0·0400	13 1 8	Very minute trace.
India (Himalaya)	Coarse-grained	60·0	0·0270	8 16 10	Distinct traces.

In every instance the gold obtained from 500 grs. of ore was not weighable, and was under 0·0002 %.

The following seven mineral species consist wholly or chiefly of sulphide of lead and antimony[1]:—

Zinckenite. $PbS+SbS^3$.—It occurs at Wolfsberg in the Harz, and in the Black Forest.

Plagionite. $4PbS+3SbS^3$, or $5PbS+4SbS^3$.—It occurs at Wolfsberg in the Harz.

Jamesonite. $2PbS+SbS^3$ (Rammelsberg); $3PbS+2SbS^3$ (Brooke and Miller).—It occurs chiefly in Cornwall; Valencia, Alcantara, Estremadura, in Spain; Arany-Idka in Hungary; Carcassone and Pont Vieux in France; Nertschinsk in Siberia; Catta-Franca in Brazil.

Boulangerite. $3PbS+SbS^3$.—It occurs at Wolfsberg in the Harz; Oberlahr, Sayn-Altenkirchen, in Rhenish Prussia; Nasafjeld in Lapland; abundantly at Molières, Department du Gard, France; Nertschinsk in Siberia; Bottino in Tuscany.

Geocronite. Schulzite. $5PbS+SbS^3$.—It occurs at Meredo in Gallicia, Spain; Sala in Sweden; Val di Castello in Tuscany. Geocronite from Sala has been found to contain 4·69% of arsenic, 1·51% of copper, 0·42% of iron, and 1·1% of zinc, and that from Tuscany to contain 4·72% of arsenic, 1·15% of copper, and 1·73% of iron.

Kilbrickenite. $6PbS+SbS^3$.—It occurs at Kilbricken, County of Clare, Ireland. It is believed by some mineralogists to be identical in composition with Geocronite.

Bournonite.—Rammelsberg assigns to it the following formula:—

$$3Cu^2S,SbS^3+2(3PbS,SbS^3)=3\left\{\begin{matrix}\frac{2}{3}PbS\\ \frac{1}{3}Cu^2S\end{matrix}\right\},SbS^3.$$

Its composition deduced from this formula is as follows:—

Sulphur	19·72
Antimony	24·71
Lead	42·54
Copper	13·03
	100·00

These numbers approximate closely to the results obtained by analysis of specimens from various localities. It occurs at Wolfsberg, Clausthal, and Andreasberg, in the Harz; Bräunsdorf and Gross Voigtsberg in Saxony; Kapnik and Neusohl in Hungary; Offenbanya in Transylvania; near Liskeard in Cornwall, where recently very fine specimens have been found, and at Beeralston in Devonshire; at Alais and Pontgibaud in France; Servoz in Savoy; Brozzo in Piedmont; in Siberia; in Potosi; Guanaxuato in Mexico.

Sulphate of lead. Anglesite. Bleivitriol (German). PbO,SO^3.—When pure it contains 68·31% of lead. It occurs beautifully crystallized in

[1] See Rammelsberg's Handbuch der Mineralchemie, 1860. Brooke and W. H. Miller's Elementary Introduction to Mineralogy, 1852. Dana's System of Mineralogy, 1854.

the prismatic system (Miller) at the mines on Parys mountain, Island of Anglesey, whence it derives its name. At those interesting and picturesque copper mines and quarries, decomposition of copper and iron-pyrites by weathering action is perpetually in operation on a large scale; and as galena, chiefly in intimate admixture with blende, is found there, the formation of anglesite as a secondary product is easily conceivable. Other recorded localities of this mineral are Leadhills and Wanlockhead in Scotland; Cumberland, Derbyshire and Cornwall; the Harz; Baden, Siegen, Tarnowitz, in Silesia; Monteponi in the island of Sardinia; Linares in Spain; Siberia; and the United States of America, at Phenixville in Pennsylvania, in Missouri, in Massachusetts, and at Rossie in the State of New York. I have superb specimens on galena from Wheatley's mine at Phenixville. A considerable quantity of ore containing lead in the state of sulphate has been imported into Great Britain from Australia. Sulphate of lead may be expected to occur wherever galena is exposed to weathering action, and is not subjected to the influence of water containing carbonate of lime in solution.

Carbonate of lead. Cerussite. White-lead ore. Weissbleierz, Bleispath (German). PbO,CO^2.—When pure it contains 77·52% of lead. It crystallizes in the prismatic system (Miller), and in nature is found both crystallized and earthy. In the latter state it is termed by the Germans "Bleierde" or lead-earth. It may be expected to occur wherever galena has been exposed to the action of atmospheric oxygen or of oxygen dissolved in water, combined with, or followed by, the action of an aqueous solution of carbonate of lime, as previously explained. It is found pseudomorphous after anglesite at Leadhills. Magnificent specimens have been met with in Cornwall. It is not necessary to enumerate special localities, as it is commonly associated with galena.

Phosphate of lead. Pyromorphite. Grün-Braunbleierz (green and brown lead ore, German).—As before stated, this mineral is not a simple phosphate, but a compound of phosphate and chloride of lead of the formula $3(3PbO,PO^5)+PbCl$. When pure it contains 75·46% of lead. It crystallizes in the rhombohedral system (Miller). It has been found at Leadhills and Wanlockhead in Scotland; and in England in Cumberland, Durham, Yorkshire, Derbyshire, and Cornwall. I have seen it raised from mines on Cromford Moor near Wirksworth, Derbyshire, under the name of "linnets," on account of its linnet-like colour. On the Continent of Europe the following localities have been recorded:—Przibram, Mies, and Bleistadt, in Bohemia; Zschoppau, Freiberg, and Johann-Georgenstadt, in Saxony; Wolfach and Hofsgrund in Baden; near Clausthal in the Harz; near Schemnitz in Hungary; Poullaouen, Huelgoët, Pontgibaud, and St. Prix, in France; Beresowsk and Katharinenberg in Siberia. In the United States of America, it has been met with at the Perkiomen mine near Philadelphia, at Phenixville, and in the State of Maine; in New York State; at Southampton in Massachusetts; and at Bristol in Connecticut.

Pyromorphite from Zschoppau in Saxony, from Altai in Siberia, and from Pontgibaud in France, has been found to contain arsenic acid, the extremes in three analyses recorded by Rammelsberg of the mineral from the three localities above-named being respectively 2·30% and 3·83%. Such minerals are regarded as isomorphous mixtures of pyromorphite and mimetesite. A little fluor-apatite has been detected in pyromorphite from the Sonnenwirbel mine at Freiberg, and from Mies and Bleistadt in Bohemia; and in a specimen from England, of which the precise locality is not given.[2] The proportions of fluor-apatite calculated by Rammelsberg from analyses of the mineral from the first two of the localities above-named are 11·64%, 6·68%, and 0·78%.

Arseniate of lead. Mimetesite.—The formula of this mineral, as before mentioned, is precisely analogous to that of pyromorphite, phosphoric acid being replaced by arsenic acid,—$3(3PbO,AsO^5)+PbCl$. When pure it contains 69·58% of lead. It crystallizes in the rhombohedral system. In England it occurs at Caldbeck Fell in Cumberland, and is known by the name of arsenio-phosphate of lead; at Wheals Gorland, Alfred, and Unity, in Cornwall; and at Beeralston in Devonshire. The localities on the Continent of Europe are Johann-Georgenstadt in Saxony; near Baden; St. Prix in France; and Nertschinsk in Siberia. The mineral from Langbanshytta in Sweden, named hedyphane by Breithaupt, is only a massive variety of mimetesite. In America compact, earthy, yellow mimetesite has been found at Argueros in Chile.

Selenide of lead, chlorides and oxychlorides of lead, lanarkite or sulphato-carbonate of lead (PbO,SO^3+PbO,CO^2), *and vanadinite (chloride of lead, combined with phosphate, and vanadiate of protoxide of lead)* are mineralogical species not of particular metallurgical interest, and for information concerning them treatises on mineralogy must be consulted.

British Lead Ores.

For the following description of the mode of occurrence of British lead ores, I am indebted to my excellent colleague Mr. Warington Smyth.

The lodes which are worked for lead in this country vary, as in fact they do in other mining districts, in structure and materials according to the character of the rock formation which they intersect, and not unfrequently with the line of their horizontal direction or strike. The great bulk of the British lead ores has from an early period been obtained from the mountain or carboniferous limestone; and about two thirds of our present annual returns are from that formation, which is extensively developed in the North of England and in Derbyshire, on a smaller scale in North Wales, and in a less notably metalliferous condition in Ireland; whilst the remaining one-

[2] See Rammelsberg's Mineralchemie, p. 57.

third is derived from veins occurring in strata of older geological periods.

As a general rule the lodes of the limestone districts have a comparatively soft matrix, large bodies of clay locally termed flucan, and dowk, often occupy a great portion of the original vein fissure, and these in many localities are found to alternate with portions of exceedingly pure and solid galena, whilst even the superficial clay, when a thick cap of that material overlies the backs of the lodes, has often yielded large amounts of ore, as in the "hushes" of the North, and in Flintshire, and as most remarkably exemplified in the "diggings" of Missouri, U.S.

When the lodes, on the other hand, exhibit less of mechanical detrital matter, and are filled chiefly by crystalline deposits, the matrix consists most abundantly of calc-spar, with which fluor-spar and barytes are variously associated,—exceedingly abundant in Northern England, almost absent in Wales,—whilst zinc-blende, or in its absence calamine, is a general concomitant, iron-pyrites comparatively unfrequent, and spathic iron ore, quartz and pearl-spar, or occasionally witherite and calamine, are confined to certain districts and zones of depth. It is to the glittering, crystal-lined "vugs" or cavernous hollows in the veins and their associated "flats" of this formation that cabinets of mineralogy owe many of their most beautiful specimens.

The general direction of the lodes is more or less east and west, although cases occur where some of the great "cross courses" or north and south veins have in particular parts, as notably near Holywell in Flintshire, yielded large amounts of ore.

The Devonian rocks, "killas," of Cornwall and Devonshire have for many years past been noted for the production of lead ores yielding a very large proportion of silver; and the structure of the lodes themselves offers many points of high interest. They are invariably found at a greater distance from the granite bosses which form so striking a feature of these counties than the tin and copper-bearing veins; and usually in killas of a softer character. A few of these lodes also take an east and west direction, coursing in some rare cases not far from lodes of tin or copper, and yet presenting a very different aspect. The majority of them, however, are cross-courses, traceable in some instances for miles, although it seldom happens that the richly lead-bearing part has been found to extend for more than a few hundred feet, or at most, fathoms in length. The associated minerals are principally fluor-spar, quartz, sometimes in a loosely granular state, often as white hornstone, bitter-spar, zinc-blende, and more rarely spathic iron ore, fahlerz, and bournonite, whilst the intersections with east and west veins have been marked by the occurrence of various ores of silver. Very notable examples of these meridional lodes have been the East Wheal Rose, Garras, the Menheniot mines, Herodsfoot, and the Tamar mines, which last were worked to a depth of 250 fathoms.

39836

The older silurian slaty country of Cardiganshire and Montgomeryshire is remarkable for the occurrence of a great number of veins having a marked east and west range, in which galena, only moderately rich in silver, is associated mostly with quartz. They carry, however, exceptionally, a little calcite, zinc-blende, witherite, and iron or copper-pyrites.

The Isle of Man displays somewhat similar rocks as a country of lead-lodes, but in this case they assume a different character, being, some of them, east and west, others north and south in their course; both classes[3] yielding a large proportion of silver in the galena. The former, as best typified at Foxdale, are heavily charged with "flucan" or with spathic iron ore, the latter, as at Laxey, with zinc-blende and copper-pyrites. An interesting peculiarity in the "Old Foxdale Mine" is that this fine lode carries in its southern part or rib a galena comparatively poor in silver, whilst the northern, at the distance of a few feet, is highly argentiferous, and sometimes shows a little silver-fahlerz. Nowhere in Europe does a good course of lead ore make a nobler show than may frequently be seen in these mines.

The series of lodes near Shelve, on the south of Shrewsbury, in the old silurian clay-slates, bounded by the Stiperstones on the east, is another example of east and west veins bearing very similar minerals to those above mentioned, with the occasional addition of the carbonate and sulphate of baryta. Several of them are accompanied on one side by a narrow dyke of porphyritic rock reminding the observer of the phenomena which attend the more fully developed mines, with their richer list of minerals, of Przibram in Bohemia.

Lastly, a group of lodes in the granite of the county Wicklow presents interesting points of comparison with the important mines of Linares, in Spain, worked in a similar rock, but they have the peculiarity of coursing in various directions, and of yielding, notwithstanding this discrepancy, very similar ores, in which the galena is attended chiefly by quartz, whilst a division of the vein is often occupied by a friable granite, not unfrequently presenting rather the appearance of having crystallized from solution than being mere disintegrated rock introduced by mechanical action.

Yield of Silver in Lead Ore from British Localities.

For the following details I am indebted to my colleague, Mr. Robert Hunt, Keeper of Mining Records at the Museum of Practical Geology. The proportion of silver is stated in troy ounces per statute ton of lead:—

[3] Two lots of ore are generally sold from Foxdale, one containing from 12 to 20 ozs., and the other from 50 to 80 ozs. of silver per ton of lead.

CUMBERLAND.

Brandlehow Mine.	ozs.	Goldscope Mine.	ozs.	Grass Field Vein Mine.	ozs.	Long Cleugh Mine.	ozs.
1860 ...	8	1856 ...	5	1854 ...	8	1861 ...	7
1861 ...	8	1857 ...	12*	1855 ...	15*	1862 ...	7
1862 ...	8	1859 ...	6	1857 ...	30*	1863 ...	7
1863 ...	8	1860 ...	4	1858 ...	30*	1864 ...	7
1864 ...	8	1861 ...	8	1860 ...	9	1865 ...	7
1865 ...	8	1863 ...	8	1861 ...	7	1866 ...	7
		1864 ...	8	1862 ...	7		
		1865 ...	8	1863 ...	7		
		1866 ...	8				

* Working on different veins or cross-courses? Otherwise the proportion of silver would not be so large.

YORKSHIRE.

Braithwaite Mine.

	ozs.
1855	7
1857	7
1859	7
1860	7
1861	7
1862	7
1865	7
1866	7

DEVONSHIRE.

Frank Mills Mine.

	ozs.
1859	6½
1860	16
1861	39
1862	28½
1863	18
1864	22½
1865	40
1866	39

CORNWALL.

Huel Mary Ann.	ozs.	Treweatha Mine.	ozs.	Trelawney Mine.	ozs.
1854 ...	63	1854 ...	84	1854 ...	46
1855 ...	66	1855 ...	71	1855 ...	44
1857 ...	62	1857 ...	66	1857 ...	47
1858 ...	66	1858 ...	63	1858 ...	50
1859 ...	63	1859 ...	65	1859 ...	55
1860 ...	65			1860 ...	64
1861 ...	63			1861 ...	63
1862 ...	74			1862 ...	63
1863 ...	65			1863 ...	69
1864 ...	71			1864 ...	71

ASSAY OF LEAD ORES.

The assays of lead ores of every kind are made in the *dry way*. Although various *wet* methods of assaying these ores have from time to time been proposed, yet not one has been found sufficiently practical for the use of smelters. The ores treated by the assayer are galena or sulphide of lead, cerussite or carbonate of lead, pyromorphite or phosphate of lead, and anglesite or sulphate of lead. In this country ores are usually designated rich when they contain 70% or more of lead.

Sampling.—The ore in every case should be reduced to powder and passed through a sieve of from 40 to 60 holes to the linear inch. Trituration may be effected in an iron mortar. After sifting, the ore should be intimately mixed, so as to ensure uniformity of composition throughout. The sample thus prepared should be gently heated to drive off moisture, or it may be dried previously to sifting; and for this purpose flat, shallow, circular or oval pans of sheet-iron or sheet-copper, 5″ or 6″ in diameter, are convenient. See fig. 4, G, p. 105.

Furnace and Implements.

Furnace.—The furnace described in the first volume of this work, in the article on the Assaying of Copper Ores by the Cornish Method, is equally suitable for assaying lead ores. It is represented in the annexed woodcut, fig. 2. Coke should be the fuel; but when not obtainable charcoal may be used.

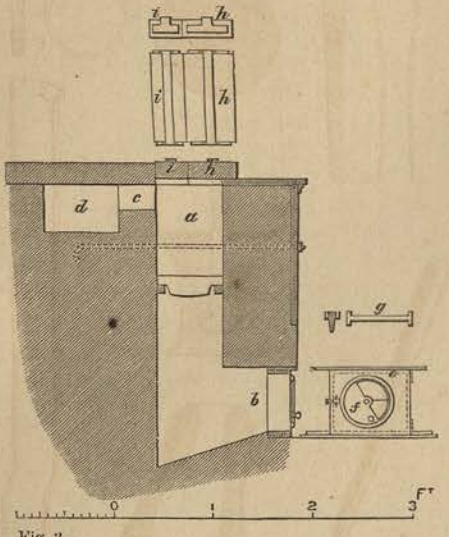


Fig. 2.

Crucibles.—Two kinds of crucibles are employed—earthen, and of wrought-iron. The varieties of earthen crucibles found to be suitable are those designated Cornish, London, Hessian, and French. Cornish crucibles, such as are used in assaying copper ores, are too wide; they should have the shape and size shown in fig. 5, E. The wrought-iron crucible which is recommended is shown in fig. 3 *a*. This recommendation is founded on long practice in the use of this crucible in the Metallurgical Laboratory of the Royal School of Mines, and on the results of numerous experiments with wrought-iron crucibles of different sizes, relative proportions and internal form. The crucible should be forged out of a short solid piece of round bar-iron by hammering it hot over a core or mandril of the same form and size as the interior of the crucible: it is better to avoid welding, as corrosion is apt to take place irregularly at the welded parts if the welding is not sound, the consequence of which may be the retention of globules of lead or even actual loss of lead by leakage.

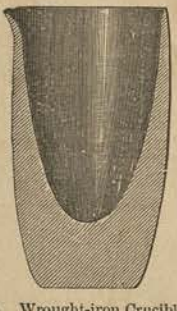


Fig. 3 *a*. Wrought-iron Crucible.

Scale 1¼″ to 20″.
Fig. 3 *b*.

Scoop.—This is required for charging the crucible, and is the same as used by copper-assayers: it is shown in fig. 4, F.

Tongs.—When earthen crucibles are used, such tongs as are shown in fig. 3 *b* will be found suitable; but in manipulating with iron crucibles, stronger tongs are required, such as are shown in fig. 5, A B.

The crucible is removed from the furnace with the tongs, B; and in pouring out its molten contents, it is held by means of the curved ends of the tongs, A, or the tongs B may be used in both operations.

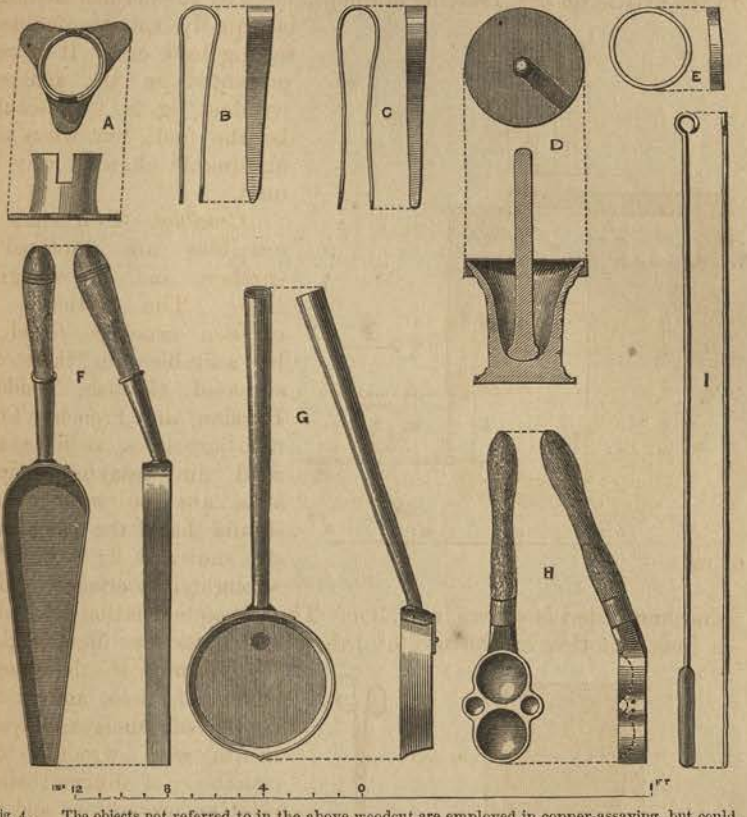
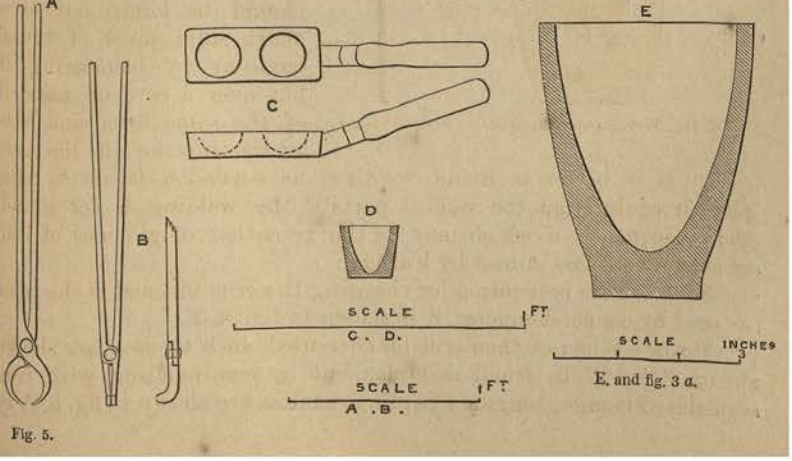


Fig. 4. The objects not referred to in the above woodcut are employed in copper-assaying, but could not be conveniently separated from the block.



E, and fig. 3 *a*.

Fig. 5.

Stirrer.—It consists of a round rod of iron, about $\frac{1}{4}''$ in diameter, flattened at one end. The copper-assay calcining rod, shown in fig. 4, I, is well adapted for this purpose.

Ingot-moulds.—Convenient and usual moulds of cast-iron are shown in fig. 5, C, D; in C there are two smooth-faced hemispherical cavities, while in D there is only one cavity, which is conical.

Hammer, forceps, and brush.—A moderately light hammer is most convenient. Suitable kinds of forceps are shown in fig. 4, B, C. The brush should be made of stiff bristles, such as in a nail or tooth-brush.

Balance and weights.—The balance should carry not less than 1000 grains, and turn at least with $\frac{1}{10}$ of a grain. No special weights are used. The produce is reported in percentage.

Fluxes and Reducing Agents.

Carbonate of Soda.—It should be anhydrous. Bicarbonate of soda may be used, but it is less convenient on account of its greater bulk for the same weight of soda. Carbonate of potash may be substituted for carbonate of soda, wholly or partially.

Borax.—It should be dried and rubbed afterwards to powder. The powder of common borax crystals may also be employed.

Fluor-spar.—It should obviously be quite free from galena or other ores of lead.

Cream of tartar or bitartrate of potash.—The commercial varieties, termed *red* and *white argol*, are commonly used.

Iron.—The reducing agent now generally adopted is wrought-iron, and for this purpose the metal in the form of hoop, rod, and nails, is suitable, but not iron-filings, of which any excess remains entangled in the reduced lead, and vitiates the result. When the iron crucible is employed, it yields the iron necessary for reduction.

Assay of Galena in Iron Crucibles with addition of Fluxes.

With iron crucibles like that previously described the assay-charges should be composed as follow:—

	I. Grains.	II. Grains.
Ore	500	500
Carbonate of soda	500	350
Borax	—	150
Argol	50	50

No. I. is suitable for rich ores comparatively free from *vein-stuff*. No. II. is adapted for what are termed poorer ores, but it is also applicable to rich ores. Although argol is not essential in the assaying of rich ores, yet its presence is advantageous, as it tends to render the atmosphere in the interior of the crucible *reducing*, and thereby to prevent or lessen the oxidation of the sulphide of iron produced in the operation; and it also aids in the reduction of any carbonate or sulphate of lead which may exist in the ore. Oxide of iron, resulting

from the oxidation of the sulphide, sticks to the sides of the crucible, and tends to retain particles of lead in pouring.

Smaller charges of ore, such as 200 grains, may be heated in crucibles of smaller dimensions than those here recommended as suitable for 500-grain charges.

The ore is mixed with $\frac{3}{4}$ or $\frac{4}{5}$ of the bulk of the flux prescribed; the mixture is placed in the fore-part of the scoop, fig. 4, F, and the rest of the flux immediately behind. The mixture of ore and flux need not be intimate, and may be made even in the scoop itself by means of a spatula. With assay-charges No. II. the borax should not be intermixed, but placed towards the back of the scoop; for, otherwise, should it contain moisture, it would froth up in the crucible and cause projection of ore. The crucible is heated to dull redness, taken out of the furnace, and then charged with the ore and flux, which are shot into it from the scoop, care being afterwards taken to brush in any particles left adherent to the scoop. The crucible, thus charged, is put back into the furnace, which should be dull red-hot, and the top of the furnace is then closed. The temperature is *gradually* raised to full redness, which occurs in about 5 minutes. *Rapid* increase of temperature might cause too quick an evolution of carbonic acid from the alkaline carbonate, and corresponding loss from projection. In the course of from 3 to 5 minutes after the temperature has risen to full redness, the contents of the crucible should be in tranquil fusion, with no sign of effervescence. The interior of the crucible, while still in the furnace, is now inspected, and any metallic globules or other matter which may be perceived sticking to the upper part should be quickly and carefully pushed down by means of the stirrer into the melted mass underneath; after which the furnace is again closed and kept so for a few minutes. The crucible is taken out of the furnace, and, after cooling a little, its contents are poured into one of the cavities of the ingot-mould, previously warmed and rubbed over with plumbago. If pouring take place as soon as the crucible is withdrawn from the furnace, especially when the temperature has been comparatively high, some lead may remain in the form of a thin film on the surface of the iron, instead of running off in globules. Immediately after pouring, the interior of the crucible is again examined; and should adherent shots of lead be observed, the crucible is held a little inclined and tapped on edge on the top of the furnace, in order to cause them to drop and coalesce at the bottom. Any lead so collected is poured into the ingot-mould by inverting the crucible. In some cases it may be necessary to proceed otherwise, and throw into the crucible, after the first pouring, about 20 or 30 grains of carbonate of soda and 5 or 10 of argol, re-heat it until complete fusion occurs, and then pour out. The time which elapses from the introduction of the charged crucible into the furnace to the final pouring usually varies from 10 to 15 minutes.

After solidification, the products of fusion are detached from the ingot-mould by inverting it; and when cold, the slag is detached

from the underlying lead, first, by tapping along the line of junction of the slag and metal, and then striking the metal sideways on an anvil or slab of iron. If, after this treatment, any particles of slag should still adhere to the surface of the lead, they may be removed by scrubbing with a brush and hot water; or dilute sulphuric acid may be resorted to for the same object. The button of lead, cleaned and dried, is now weighed, along with any globules which may have been collected; and from the quantity found the percentage or *produce* is calculated.

The slag, from No. I. assay-charge, is comparatively hard; and its fracture is compact, fine-grained, black, and dull. The slag, from No. II. assay-charge, is more tender and brittle than that from No. I.; and its fracture is compact, granular-crystalline, black, and vitreous or resinous in lustre. Both kinds of slag vary somewhat in external characters, according to the nature of the foreign matter in the ore; and they often contain cavities in the centre. As soon as the button of lead is cold, the slag should be detached; otherwise, it quickly absorbs moisture from the air, and becomes somewhat soft, which renders its separation from the lead more difficult. The reduced lead should be soft and malleable. When the lead appears more or less extruded over the surface of the slag, and is not collected into a well-formed button, it is a sign either of bad pouring or of the ingot-mould having been too cold. The purest galena yields by this method of assaying, when conducted in the most skilful manner, from 84¼% to 85¼% of lead, the percentage of lead in pure sulphide of lead being 86·61%.

From long experience of this method of assaying in the Metallurgical Laboratory of the Royal School of Mines, and from an experimental comparison of it with other methods, we have come to the conclusion that it is the best. Its advantages are general suitableness for all classes of lead ores, facility in manipulation, shortness of time, and approximate accuracy. One crucible will suffice for 15 or 20 assays. Well-made crucibles are, however, expensive; but in large numbers they might be produced at a tolerably low price. I do not know who first proposed and used iron crucibles in the assaying of lead ores. I received my first information concerning this process in 1851 from the late Mr. James Barker, of the Alport Lead-smelting Works, Derbyshire, who also presented me with specimens of the crucibles there and then in use. The iron-crucible method has now become general in British lead-smelting works; and we know that lead-assayers who have received instruction at the above-mentioned school have long since introduced that method into works with which they are connected.

Assay of Galena in Iron Dishes.

This method was generally in use in Wales; but in some places in the Principality it has been displaced by the iron-crucible method. I saw it practised at lead works near Holywell, Flintshire, in the

following manner. The apparatus consists of a dish-shaped vessel of wrought-iron such as is shown to scale in fig. 6, provided with a hollow hemispherical cover of iron, somewhat larger in diameter than the cavity in the dish. It is fashioned by hammering hot a square piece of wrought-iron plate so as to form a round, shallow, cup-like cavity, 5″ in diameter and 1″ in depth at the centre. A groove or channel, A A, is made on each side, for convenience in pouring out the reduced lead. Iron is the reducing agent, and, as in the iron-crucible method, it is supplied by the dish itself. The assayer was a blacksmith, and he was reported to be more skilful in the assaying of lead ores than at his own trade. The sample of ore operated upon weighed 10 ounces troy, the usual quantity.

The dish is heated to bright redness on a blacksmith's fire, the ore is put into the cavity, and the cover is immediately afterwards adjusted. The fire is urged by the bellows for about 2 minutes, when the dish is removed and put on an iron ring for support ; the cover is taken off, and as fast as the so-called *slurry*, which for the most part is regulus of sulphide of iron, solidifies on the top of the molten lead, it is carefully pushed away with a pointed stick from the side of the cavity, where the assayer intends to pour from, so that the metal may run out with a clean bright surface. When all the *slurry* has become solid, the lead is poured into a conical ingot-mould of bronze. After pouring, the dish is fitted with its cover and replaced on the fire, which is urged strongly. Any scale or matter adhering to the sides of the cavity is detached and pushed towards the centre, and the contents are well stirred. When the *slurry* is thoroughly melted, it is poured into an iron ingot-mould with a conical cavity. When cold, a small button of lead will be found at the bottom, and this is detached, freed from any adherent matter by tapping it with a hammer, and added to the other button of lead. The first fusion occupied 5 minutes, from the time the ore was put into the dish to the time it was poured out ; and the second or re-melting of the *slurry* occupied 6 minutes. The assay produce of the ore was about 75%. Some ores smelted at these works yielded as much as 82% of lead by the dish process. Double assays are always made, and the

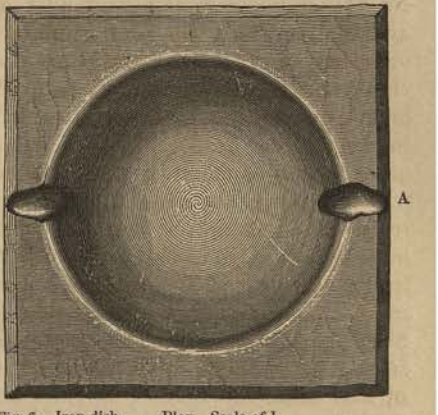


Fig. 6. Iron dish. Plan. Scale of $\frac{1}{3}$.

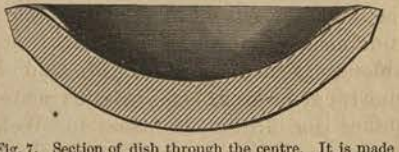


Fig. 7. Section of dish through the centre. It is made thicker towards the bottom of the cavity.

results seldom differ from each other by more than 1 dwt. No flux is used with rich ores. To poor ores, which do not melt completely (into lead and *slurry*), a little carbonate of soda is added to the contents of the dish when heated, in order to produce the requisite liquidity. There are, however, poor ores (generally of the oxidized class) which do not need such addition. The quantity of lead operated upon is convenient for calculation, as lead ores are always estimated according to the percentage of lead. The corners of the dish are well suited for grasping firmly with tongs. By the addition of black-flux a higher produce may be obtained, but it is never used. The lead obtained in the second pouring varies in weight from 2 to 10 dwts. As an example of actual results, the following is given:—

	ozs.	dwts.
Weight of ore (troy)	10	0
Do. lead from first pouring	7	12
Do. do. second pouring	0	9
	8	1

8 ozs. 1 dwt. × 10 = 80½ ozs., the percentage of lead sought.

Assay of Lead Ores in Iron Crucibles without Fluxes.

In South Wales the process is conducted as follows. An iron crucible is used of the following dimensions: diameter at the top, $2\frac{5}{8}''$, at the bottom, $2\frac{1}{2}''$; height, $2\frac{3}{4}''$, outside measure; thickness of the sides at the top, $\frac{5}{16}''$; of the bottom, $\frac{5}{8}''$. The weight of ore submitted to assay is 2½ ounces (troy). The weighed ore is transferred to the crucible by the aid of a copper scoop. The crucible and its contents are heated in an air-furnace to a temperature sufficient for the complete fusion of the sulphide of iron, resulting from the decomposition of the galena. The fused products are poured out into a convenient ingot-mould; and when cold the regulus is detached, and the button of lead cleaned and weighed in the manner before specified. The time required for the assay is from 10 to 15 minutes. Best ores yield from 81% to 82% of lead by this method. At the works at which this process is practised, the samples of lead ores are also submitted to the method of assay with the addition of fluxes, in iron crucibles, of somewhat larger dimensions than above stated.

Assay of Lead Ores in Earthen Crucibles, with addition of Iron.

The same mixtures of ore and fluxes, as previously described (p. 106), are used. The ore is mixed with from ¾ to ⅘ of the bulk of flux, and put into a cold crucible. The residual flux is spread on the top of the mixture, and then one or two pieces of wrought-iron are pressed into the latter so as to reach the bottom of the crucible. The crucible, thus charged, is placed in the furnace, which should be dull red-hot, and coke is packed well round the outside up to the top of the crucible, after which a cover is fitted on the latter, and the fur-

nace closed above. The temperature should be gradually raised, as in the case of iron crucibles, and for the same reason. During the process, the iron should be stirred about once or twice, and inverted in the molten mass, in order to remove any particles of ore which may have been projected on, and have adhered to, the outstanding parts; and while this manipulation is going on, the top of the furnace is only partially opened, with a view to prevent the crucible from being too much cooled. When the contents of the crucible are in tranquil fusion, the iron is taken out and examined while hot, and should any shots of lead be found adherent to it, they must be washed off by immersing it in the molten slag, after which it is withdrawn, and the crucible, with its cover on, is left in the furnace for a few minutes longer. The crucible is then removed from the furnace, and its contents are poured into the ingot-mould; and as soon as cold, the slag is detached and the button of lead cleaned in the manner previously described. The time required in this method of assaying varies from 20 to 25 minutes.

The slag resembles that which is produced in assaying in the iron crucible with the addition of fluxes, but is usually more vitreous, from the presence of silicate of soda resulting from the action of the soda during fusion upon the siliceous substance of the crucible. The button of lead should be perfectly clean, soft and malleable; but, on the contrary, should it be comparatively hard and present in a greater or less degree the colour and lustre of galena, and should there be a metallic film of similar character attached to the under surface of the slag, the assay is worthless, as these signs indicate incomplete reduction of the ore, owing probably to deficient heat during the process. Near approximation in weight in the quantities of lead obtained in two or more assays is not to be regarded as conclusive evidence of accuracy; for, when the temperature has been insufficient, such approximation may occur, and yet the produce be uniformly too low. The yield of lead from the purest galenas by this process ranges from 82% to 83%. The quantity of iron actually used in practice is much greater than theoretically would suffice for the complete reduction of the sulphide of lead operated upon. A piece of hoop-iron, bent in the form of the letter U, with about 1″ between the opposite surfaces, from $\frac{1}{16}$″ to $\frac{1}{20}$″ thick, from $\frac{7}{8}$″ to 1″ wide, and from 2″ to 3″ long, is suitable for the purpose. This U-piece of iron may be employed in the following ways. It may be inserted with the ends downwards, in which case the corners should be previously cut or broken off, so as to allow as much of the iron as possible to touch the bottom of the crucible; if the iron be too thin or the sides of the U be too near each other, the lower portions may become so thin by corrosion during the process as to be liable to come together and so entangle globules of metal between them. The U-piece of iron may be inserted with the ends uppermost, in which case the lower or rounded portion is liable to be eaten away, and leave detached pieces of iron in the crucible, which may retain some of the lead during pouring. Instead of a U-piece of iron, two pieces, each about 3″ long, may be placed

opposite each other, and inclining towards the bottom of the crucible. When iron nails are used, about four of them, 3″ long each, are placed in the crucible crosswise, with their heads downwards and slanting towards the bottom. When rod-iron is used, it should be about ¼″ in diameter, and of about the same length as the nails. The use of both nails and rod increases the trouble of the manipulation, and the yield of lead is somewhat less than what is obtained by means of hoop-iron.

Assay of Carbonate and Phosphate of Lead.

In assaying these ores, earthen crucibles are used, and although iron is not needed as a reducing agent, yet its presence is not objectionable. The following assay charges are prescribed :—

	I. Grains.	II. Grains.	III. Grains.
Ore	300	300	500
Carbonate of soda	400	350	500
Charcoal powder	20	—	—
Argol	—	100	100
Borax	30	30	30

Nos. I. II. are applicable to phosphate, and No. III. to carbonate, of lead. The method of assaying is similar to that practised in earthen crucibles, with the addition of iron, and similar crucibles are also employed. The slags produced in assaying phosphatic ores are vitreous, more or less opaque, greyish-white, dark-grey or black; they should not be green or yellowish-green, as such colours indicate incomplete reduction. The slags produced in assaying ores of carbonate of lead are tender and easily frangible; and their fracture is fibrous, crystalline, and dark-grey. An assay of phosphatic ores is completed in from 25 to 30 minutes, *i.e.* from the introduction of the charged crucible into the furnace to its withdrawal, and the pouring out of its contents. Towards the end of the process, the temperature should be kept up, and pouring should be quickly effected; for, otherwise, the slag, which consists chiefly of phosphate of soda, will run comparatively thick. The time usually occupied in an assay of ores of carbonate of lead is about 20 minutes. Ores both of phosphate and carbonate of lead may be assayed in earthen crucibles, with the addition of iron and fluxes, as previously described; and, indeed, by means of this method, a somewhat greater percentage of lead is obtained. When arseniate of lead is associated with phosphate of lead, the presence of iron is essential in order to decompose any arsenide of lead which may be generated.

Ores of sulphate of lead cannot be properly assayed with the addition of the above-mentioned fluxes without the presence of iron, because the slag is liable to be impregnated with double sulphide of sodium and lead formed in the operation.

The assays of all these oxidized ores may be made in the iron crucible with the addition of flux No. II. p. 106; but less borax will generally suffice, and this substance becomes a costly item in large assaying operations. Borax, however, should always be present in

order that this method may be applicable to all kinds of ores. In practice it is obviously desirable that every kind of ore should, as far as possible, be assayed by one method.

Influence of Non-metalliferous Matters upon the Yield of Lead by the method of Assay with Fluxes in the Iron Crucible.

The difference between the quantity of lead obtained by assaying in iron crucibles with fluxes, and the actual quantity in the ore, is nearly the same for ores of the highest produce down to ores containing about 50% of lead; and in ores containing less than 50% of lead, the difference is much less than is sometimes stated. Silica appears to have more influence on the yield of lead than carbonate of lime or sulphate of baryta, probably because a higher temperature is required to flux the silica in the first stage of the operation. The presence of such matters as lime and oxide of iron tend to lessen the loss of lead in the presence of silica.

The following experiments were made with a view to ascertain the influence of various substances when associated with galena upon the yield of lead by dry assay with fluxes in the iron crucible. The same galena was used in all the succeeding experiments and found by analysis to contain 85·70% of lead.

Carbonate of Lime.

	Weight, grains.		Proportion per cent.	
	Galena.	Carbonate of lime.	Galena.	Carbonate of lime.
I.	50	450	10	90
II.	100	400	20	80
III.	150	350	30	70
IV.	200	300	40	60
V.	250	250	50	50
VI.	300	200	60	40
VII.	350	150	70	30
VIII.	400	100	80	20
IX.	450	50	90	10
X.	500	—	100	—

The carbonate of lime used was white marble in powder, which had been passed through a sieve of 80 holes to the linear inch. In each experiment the ore and carbonate of lime were weighed separately in a balance turning with $\frac{1}{100}$ of a grain, and then intimately mixed with about $\frac{4}{5}$ of the bulk of the fluxes; the mixture was placed on the assay scoop, and the remaining portion of fluxes immediately behind, as previously directed; and the whole was then projected into the hot iron crucible, and the assay conducted with the usual precautions. The experiments were made in the order above stated. The fluxes used in each case were—

	Grains.
Carbonate of soda (dried)	350
Borax (calcined)	150
Argol	50

In experiments I. II. III. the time occupied was from 15 to 20 minutes, and in experiments IV. to X. inclusive, from 10 to 15 minutes. The mixtures melted easily, leaving the sides of the crucibles clean. The slags were liquid, except in experiments I. II., in which, as they were somewhat pasty, about 50 grains of borax were subsequently added. The mixtures containing most lime required to be poured *hot* in order to prevent setting. Any globules left in the crucible after pouring were removed, but it was not found necessary to add more flux to effect their removal. The slags were compact, close-grained, black, and dull; and they adhered somewhat to the buttons of lead except in experiment X., in which the slag presented the usual characters. As the slag from No. 1. did not possess sufficient fluidity to allow the lead to collect properly, the experiment was repeated with the following proportion of fluxes :—

	Grains.
Borax	250
Carbonate of soda	250
Argol	30

The buttons of lead were cleaned in the ordinary manner. The results are as follow :—

	Weight of lead obtained.	Percentage of lead obtained.	Percentage of lead present.	Loss of lead on 100 parts of the mixture of galena and carbonate of lime.	Lead calculated for 100 parts of galena.	Loss of lead on 100 parts of galena.	Silver obtained.	Silver calculated for 100 parts of galena.
	Grains.						Grains.	
I.	38·9	7·78	8·57	0·79	77·80	7·90	0·016	0·032
II.	80·1	16·02	17·14	1·12	80·10	5·60	0·032	0·032
III.	120·5	24·10	25·71	1·61	80·30	5·40	0·050	0·033
IV.	166·6	33·32	34·28	0·96	83·30	2·40	0·070	0·035
V.	206·9	41·38	42·85	1·47	82·80	2·90	0·088	0·035
VI.	251·6	50·32	51·42	1·10	83·50	2·20	0·108	0·036
VII.	293·8	58·76	59·99	1·23	83·90	1·80	0·130	0·036
VIII.	336·0	67·20	68·56	1·36	84·00	1·70	0·137	0·034
IX.	377·5	75·50	77·13	1·63	83·90	1·80	0·161	0·036
X.	421·8	84·36	85·70	1·34	84·36	1·34	0·180	0·036

SILICA.

	Weight, grains.		Proportions per cent.	
	Galena.	Silica.	Galena.	Silica.
I.	50	450	10	90
II.	100	400	20	80
III.	150	350	30	70
IV.	200	300	40	60
V.	250	250	50	50
VI.	300	200	60	40
VII.	350	150	70	30
VIII.	400	100	80	20
IX.	450	50	90	10
X.	500	—	100	—

White glassmakers' sand, passed through a sieve of 80 holes to the linear inch, was employed. The ore and silica were weighed out separately, and mixed as in the previous experiments with carbonate of lime. The fluxes employed in each experiment were:—

	Grains.
Carbonate of soda	500
Argol	50

The time occupied in each experiment was about 15 minutes.

No. I. Although the temperature was very high, yet the mixture softened with difficulty, and was attended with loss of lead by vaporization; 150 grains of carbonate of soda were added in order to complete the fusion, but the product poured thick from the crucible. The slag was vitreous and black, and the button of lead was easily separated from it.

No. II. Fusion occurred as in No. I.; it was necessary to add 100 grains of carbonate of soda to cause sufficient liquidity for pouring, and the product poured thick. The slag resembled that of No. I.

No. III. Fusion occurred as in No. I; 100 grains of carbonate of soda were added to increase liquidity, and the slag resembled that in No. I.

No. IV. The mixture melted properly; the slag was vitreous towards the exterior and black; the centre was dull and coarse-grained.

Nos. V.–X. The mixtures melted easily; in Nos. V., VI., VII., the slags were granular and dull; and in Nos. VIII., IX., X., they were hard, fine-grained, and dull.

No regulus was observed in any of the products. The buttons of lead were cleaned in the usual way. The results are as follow:—

	Weight of lead obtained.	Percentage of lead obtained.	Percentage of lead present.	Loss of lead on 100 parts of the mixture of galena and silica.	Lead calculated for 100 parts of galena.	Loss of lead on 100 parts of galena.	Silver obtained.	Silver calculated for 100 parts of galena.
	Grains.						Grains.	
I.	25·3	5·05	8·57	3·51	50·60	35·10	0·005	0·010
II.	71·9	14·38	17·14	2·76	71·90	13·80	0·027	0·027
III.	112·1	22·42	25·71	3·29	74·70	11·00	0·043	0·026
IV.	156·8	31·36	34·28	2·92	78·40	7·30	0·054	0·032
V.	200·2	40·04	42·85	2·81	80·10	5·60	0·086	0·04
VI.	245·3	49·06	51·42	2·36	81·77	3·93	0·100	0·033
VII.	286·5	57·30	59·99	2·69	81·86	2·84	0·120	0·034
VIII.	331·7	66·34	68·56	2·22	82·92	2·78	0·137	0·034
IX.	380·6	76·12	77·13	1·01	84·52	1·18	0·160	0·035
X.	421·3	84·26	85·70	1·34	84·26	1·34	0·170	0 034

No. III. was repeated with the following proportions of fluxes:—

	Grains.
Borax	150
Carbonate of soda	250
Argol	50

The mixture melted more easily and quietly than in the preceding experiments; the slag was more liquid, and a little lead-coloured flame was observed at the commencement; no regulus was produced. The lead weighed 111·6 grains = 74·4% of lead, and contained of silver ·049 grains = ·033% of the weight of the galena.

Experiments Nos. I., II., III., were repeated. Assuming that the loss of lead was chiefly owing to want of sufficient liquidity in the products, the experiments were repeated with the following proportions of fluxes :—

	Grains.
Carbonate of soda	1000
Argol	50

Fusion took place readily, the slag was comparatively thin and liquid, and poured out clean from the crucible without leaving globules of metal. The slag in No. I. was somewhat vitreous, opaque, black, and dull, and near the upper part somewhat crystalline. The slags in Nos. II., III., were granular, crystalline, and greenish-black. The results are as follow :—

	Weight of lead.	Percentage of lead obtained.	Percentage of lead present.	Loss of lead on 100 parts of the mixture of galena and silica.	Lead calculated for 100 parts of galena.	Loss of lead on 100 parts of galena.	Silver obtained.	Silver calculated for 100 parts of galena.
	Grains.						Grains.	
I.	32·5	6·50	8·57	2·07	65·0	20·7	0·012	0 024
II.	78·4	15·68	17·14	1·46	78·4	7·3	0·034	0·034
III.	117·9	23·58	25·71	2·13	78·6	7·1	0·052	0·035

SULPHATE OF BARYTA.

	Weight, grains.		Proportions per cent.	
	Galena.	Sulphate of baryta.	Galena.	Sulphate of baryta.
I.	100	300	25	75
II.	200	200	50	50
III.	300	100	75	25

The sulphate of baryta was in fine powder. Fluor-spar has the property of forming very liquid products when heated with sulphate of baryta in certain proportions, and it was employed to the extent of half the sulphate of baryta present. The quantities employed in Nos. I., II., and III., were :—

	I.	II.	III.
	Grains.	Grains.	Grains.
Fluor-spar	150	100	50
Carbonate of soda.....	250	300	350
Argol	30	30	30

Intimate mixture with the ore was made in each case, and the fusion conducted in iron crucibles as in the previous experiments. The

mixtures melted easily and quietly; the products became thin and liquid at the end of the operations, and were poured out clean from the crucible. The slags were more or less opaque, granular, dull, greenish-black, and crystalline towards the centre; they adhered somewhat to the buttons of lead, and they were tender and easily frangible, the frangibility increasing with the proportion of fluor-spar. No regulus was observed in any of the products. The buttons of lead were cleaned in the usual way. The results are as follow:—

Weight of lead.	Percentage of lead obtained.	Percentage of lead present.	Loss of lead on 100 parts of the mixture of galena and sulphate of baryta.	Lead calculated for 100 parts of galena.	Loss of lead for 100 parts of galena present.	Silver obtained.	Silver calculated for 100 parts of galena.
Grains.						Grains.	
79·4	19·85	21·43	1·58	79·4	6·30	—	—
167·5	41·88	42·85	0·97	83·75	1 95	0·068	0·034
254·6	63·65	64·27	0·62	84·87	0·83	0·105	0·035

Influence of Metals upon the Method of Assay with Fluxes in the Iron Crucible.

Silver.—During the assay, practically the whole of the silver passes into the lead; but the quantity is generally insufficient to add materially to the weight of the lead obtained. Moreover, supposing it to be present to a greater extent, it is customary to report the lead as containing silver; and, therefore, the total weight of lead obtained by assay would be reported inclusive of the silver present.

Gold.—This metal is always present in lead ores, but generally in unweighable quantity on the amount of ore operated on; and it may be practically disregarded.

Copper.—This metal is sometimes present in lead ores in the state of copper-pyrites, grey copper ore, or carbonate of copper. During the assay, part of the copper passes into the lead and part remains in the slag, the quantity which passes into the lead varying according to the nature of the associated cupriferous minerals and the nature and proportion of reducing agents employed. The following experiments were made upon galena in admixture with copper-pyrites. The galena operated on contained 85·15% of lead by dry assay, and the copper-pyrites 31·42% of copper.

	I.	II.	I.	II.
	Weight, grains.		Per cent.	
Galena	450	375	90	75
Copper-pyrites	50	125	10	25

The fluxes employed were:—

	Grains.
Borax	150
Carbonate of soda	350
Argol	50

The weighed quantities of galena and pyrites were finely powdered and intimately mixed, and afterwards intermixed with the fluxes.

The assays were made in the usual manner. The results are as follow:—

	Weight of lead obtained.	Cupriferous lead per cent.	Percentage of lead obtainable from galena free from copper ore.
	Grains.		
I.	382	76·4	76·6
II.	318·5	63·7	63·5

The lead buttons were somewhat harder than buttons free from copper, and had a lead-grey fracture. The slags resembled those obtained in assaying ordinary galena. Portions of the buttons were submitted to analysis.

I. 101·2 grains contained 1·19 grain of copper; the button of lead therefore contained 4·49 grains of copper, or 0·90% of the ore-mixture.

II. 101·7 grains contained 3·81 grains of copper; the button of lead therefore contained 11·93 grains of copper, or 2·39% of the ore-mixture.

From the foregoing data the following percentage results have been calculated:—

	I. Per cent.	II. Per cent.
Total weight of copper present.....	3·14	7·85
Lead button contained of { Lead	75·50	61·31
Lead button contained of { Copper.....	0·90	2·39
Copper present in the slags	2·24	5·46

The presence of copper would become manifest in the subsequent cupellation of the button of lead, as it imparts a greyish-black or black colour to the cupel.

Zinc.—This metal is sometimes present in lead ores in the state of blende or calamine. During assaying part of the zinc is volatilized, and part remains in the slag, and only a very small portion passes into the lead. The following experiments with blende have been made. The galena operated on was the same as that used in the experiments with copper-pyrites. The blende contained 55·84% of zinc.

	I.	II.	I.	II.
	Weight, grains.		Per cent.	
Galena	450	375	90	75
Blende	50	125	10	25

The substances were mixed, and the same fluxes used as in the previous experiments with copper-pyrites. The assays were made in the usual manner; and during the process the vapour of zinc was observed, and mostly in II. The results are as follow:—

	Weight of lead obtained.	Lead per cent.	Percentage of lead obtainable from galena free from blende.
	Grains.		
I.	381·1	76·20	76·6
II.	305·8	61·16	63·5

Portions of the buttons were analysed.

I. 159·4 grains contained 0·06 grain of zinc; the button of metal therefore contained 0·14 grain of zinc, or 0·03% of the ore-mixture.

II. 131·4 grains contained 0·14 grain of zinc; the button of metal therefore contained 0·33 grain of zinc, or 0·06% of the ore-mixture.

From the foregoing data the following percentage results have been calculated:—

		I. Per cent.	II. Per cent.
Total weight of zinc present		5·59	13·96
Lead button contained of	Lead	76·17	61·10
	Zinc	0·03	0·06
Zinc in the slag and volatilized		5·56	13·90

Antimony.—This metal is generally present in lead ores, in the state of sulphide. During assaying a large proportion of the antimony passes into the lead. The following experiments have been made. Picked specimens of native grey sulphide of antimony were used, which when pure contains 71·93% of antimony.

	I. Weight, grains.	II. Weight, grains.	I. Per cent.	II. Per cent.
Galena	450	375	90	75
Sulphide of antimony	50	125	10	25

The assays were made in the same way, and with the same proportion of fluxes as in the foregoing experiments. The results are as follow:—

	Weight of antimonial lead obtained.	Antimonial lead per cent.	Percentage of lead obtainable from galena when free from sulphide of antimony.
	Grains.		
I.	413·5	82·7	76·6
II.	367·5	73·5	63·5

The buttons of lead were harder and whiter than those obtained from ordinary galena; their fracture was bright and granular. The theoretical amounts of antimony present in I. II. are 7·19 and 17·98 respectively, which added to the weight of lead obtainable from ore free from antimony, give a total of 83·79% and 81·48% respectively, of antimonial lead.

Arsenic.—This metal is sometimes present in lead ores in the state of arseniate of lead, or arsenical iron-pyrites. During assaying part of the arsenic is volatilized in the state of arsenic or sulphide of arsenic, and part enters into combination with iron, and separates on cooling on the top of the lead as speise, or arsenide of iron, of the formula Fe^6As, which may be detached from the lead by hammering. The lead is practically free from arsenic.

Iron.—This metal is sometimes present in lead ores in the state of iron-pyrites. During assaying it passes into the slag, forming a double sulphide of iron and sodium, and does not exert any marked influence on the yield of lead.

Wet Assay of Lead Ores.

Several methods have been proposed for the estimation of lead, by means of standard solutions; but so far as we are aware, none have been successfully applied in the assaying of ores of lead. They either fail in requiring too much expenditure of time, from inaccuracy of the method, from interference of substances often existing in lead ores, or from other causes. We believe that the dry method of assaying must always be resorted to as the only direct, accurate, and practical method of quantitatively estimating the silver in lead. Some of these methods have been tried in our metallurgical laboratory during many months, and have been abandoned on account of one or more of the objections above specified. A description of a wet method of assaying lead ores practised at Bleiberg will be found at p. 270.

EXTRACTION OF SILVER FROM LEAD.

THE processes employed in the extraction of silver from lead are distinct and complete in themselves; and, as it will be necessary to refer to them frequently in the sequel, they may, it appears to me, be most conveniently described in this place. The processes in question are as follow :—

I. Desilverization by crystallization, or Pattinson's process.
II. Desilverization by zinc, or Parkes' process.
III. Cupellation.

PATTINSON'S PROCESS.

Before Mr. Hugh Lee Pattinson appeared, silver was always directly extracted from lead by the process of cupellation, which is founded on the rapid oxidizability of lead when heated with free access of atmospheric air, say to the melting-point of its protoxide, and on the non-oxidizability of silver under those circumstances. It was generally considered that cupellation could not be profitably conducted in the case of lead containing less than 8 ozs. of silver in the ton; and as a large quantity of lead is produced which contains silver in less, though still very notable, proportion, the loss of that precious metal was exceedingly great. By Pattinson's process silver can be extracted with profit from lead when present only in the small proportion of 2 or 3 ozs. to the ton of lead. To Mr. Pattinson, therefore, the world is indebted for a most valuable and, in a metallurgical point of view, most interesting invention, which everywhere bears the name of its author. The Germans have made the verb "pattinsoniren," and the verb pattinsonize may with equal propriety be employed in English. The French have made the substantive "pattinsonage" to designate the process.

Mr. Pattinson was of humble parentage and born at Alston, in Cumberland, where he was employed professionally as lead-assayer to the Commissioners of Greenwich Hospital; and he died at Newcastle-upon-Tyne, November 11th, 1858. He was a self-made, observant, ingenious, clear-headed, upright man, whom I knew personally well, and whose memory I much respect. He communicated a paper on the history and nature of his process to the British Association in 1838, which was printed in full in their transactions. He obtained a patent for this invention, dated October 28th, 1833 (No. 6497), and entitled "An improved method of separating silver from lead." He

told me that he gained 16,000*l.* by this invention, not a large sum considering the wealth which it has conferred upon many other persons. He further assured me that not long after its introduction, it added 5000*l.* a-year to the income of a certain lead-smelter in the north, who nevertheless grudged the inventor even his comparatively very small share of the profit!

His first notion, he tells us, was to distil lead in the hope that, owing to the wide difference between the melting-points of lead and silver, the former might evaporate and the latter remain fixed. On this subject he records the following experiment: Two or three pounds of lead, granulated by being fused and poured into water, were introduced into a stone-ware retort well coated with very refractory luting, a little coarsely-powdered charcoal being added, to prevent the formation of oxide and its consequent action upon the retort. The retort being built into a furnace, with a powerful double bellows attached, and its beak immersed in water, was most intensely heated for several hours, at the end of which the furnace was suffered to cool. The retort, on examination, was found to have been quite in a soft state from the intense heat to which it had been exposed, and in this half-melted condition to have sunk down upon the stand supporting it in the furnace, so that its lower part was bulged in, like that of the bottom of a wine bottle. It had remained, however, perfectly air-tight; and in the upper part of its neck were found a number of minute globules of lead, which had evidently risen in vapour and been condensed; but the quantity was far too little to allow of its being tested for silver. Many subsequent experiments were made to obtain distilled lead in greater abundance without success, as in every case either the retort failed, or the heat proved insufficient to vaporize the metal. This experiment, therefore, merely established the fact, of which from analogy there was indeed little doubt, that lead can be raised in vapour and again condensed like mercury, zinc, and some other metals, leaving the question, whether silver does or does not rise along with it, still unsettled; it showed, also, however, that the distillation of lead in the large way is quite impracticable, owing to the intense heat for its conversion into vapour.

The next idea was, that as the specific gravity of silver is something less than that of lead, there might possibly be a tendency in the silver to rise up to the top of a mass of lead, kept melted a long time, at a uniform temperature, and perfectly at rest. This simple experiment was, therefore, tried repeatedly in variously shaped vessels; but in no instance was there the least trace of any separation. Various other experiments were tried, both in the dry way and by the application of liquid menstrua, all of which were unsuccessful; but during their prosecution in the month of January, 1829, Mr. Pattinson required lead in a state of powder, and to obtain it, adopted the mode of stirring a portion of melted lead in a crucible, until it cooled below its point of fusion, by which the metal is obtained in a state of minute subdivision. In doing this he was struck with the circumstance that, as the lead cooled down to

nearly its fusing-point little particles of solid lead made their appearance, like small crystals among the liquid lead, gradually increasing in quantity as the temperature fell. After observing the phenomenon once or twice, he began to conceive that possibly some difference might be found in the proportions of silver held by the part that crystallized and the part that remained liquid. Accordingly, he divided a small quantity of lead into two portions, by melting it in a crucible and allowing it to cool very slowly with constant stirring, until a considerable quantity crystallized as already mentioned, from which the remainder while still fluid was poured off: an equal weight of each was then submitted to cupellation, when the button of silver from the liquid lead proved to be very much larger than that from the crystallized lead; and thus the somewhat curious fact was discovered, that fluid lead, holding silver in solution, suffers a portion to escape from it, under certain circumstances, in the act of becoming solid. The lead used in the original experiment was what is considered rich in silver; it contained 40 ozs. 15 dwts. 8 grs. per ton. and was divided into a crystallized portion found to contain 25 ozs. 4 dwts. 21 grs., and a fluid portion holding 79 ozs. 11 dwts. 12 grs. per ton, the latter being necessarily much smaller than the former in quantity. The experiment was repeated a great number of times upon lead of every variety as to content of silver with the same general result; but being always performed in a crucible upon small quantities of lead, which of necessity cooled quickly, the crystallized portion was never entirely deprived of its silver, nor, indeed, reduced below 2 or 3 ozs. per ton.[1]

If my memory does not deceive me, Mr. Pattinson told me that he accidentally dropped a crucible containing lead which had partially solidified, the still liquid portion running out upon the floor. He assayed both portions and found that the liquid contained notably more silver than the solid portion.

Mr. Pattinson states that it was not until the spring of 1833, that he was so circumstanced as to be able to apply on the large scale the principle which had thus been discovered. He then introduced the system of large cast-iron pots, which is essentially the same as that ever since in use. At this period he was not satisfied with the method of concentrating the silver in a comparatively small portion of the lead operated upon; and, accordingly, he attempted to arrive at the same result with much less expenditure of time and labour. He conjectured that the crystals would be rendered much poorer in silver if they could be more thoroughly drained of the liquid lead. With this view he subjected the crystals removed by means of a perforated ladle to a cautiously regulated heat in a reverberatory furnace; and so he succeeded in obtaining in one operation from lead originally holding 12 ozs. of silver per ton, 4 parts of poor lead containing about ¾ oz. of silver per ton, and 1 part of rich lead containing 50 ozs. per ton. This process, he informs us, was effected at a moderate

[1] I have recorded these experiments in Mr. Pattinson's own words.

expense and with but little loss of lead; and was for some time carried on at various lead works in the kingdom. But this re-heating of the crystals rendered necessary a peculiar and rather expensive apparatus, and it was moreover found difficult of management. The workmen could not always keep the temperature of the

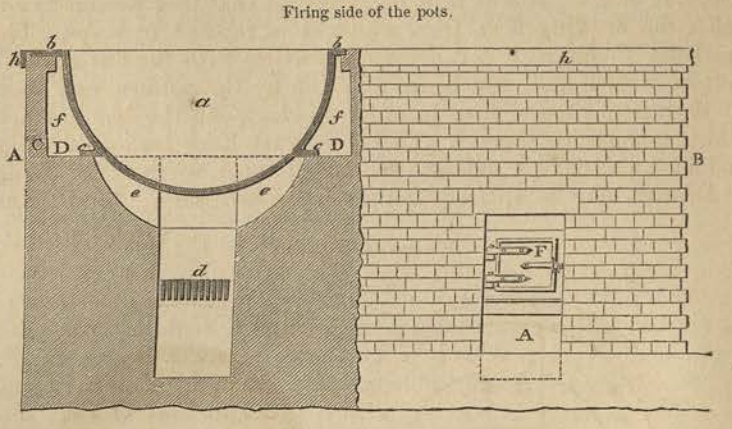


Fig. 8. The right half is the end elevation at the fire-door; and the left half is a vertical section through the centre of the pot and across the fire-bars.

furnace at the right degree; and it often happened that the crystals were wholly melted down. Further, the lead in the form of crystals rapidly oxidized, and the subsequent reduction of the oxide was attended with loss of lead. From the foregoing objections to what Mr. Pattinson designates the "draining process," he was induced finally to adopt and recommend the system of repeated crystallization in cast-iron pots.

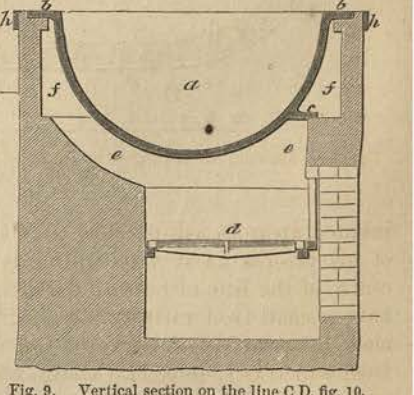


Fig. 9. Vertical section on the line C D, fig. 10.

Description of the apparatus. —I am indebted to Mr. John Henry, formerly manager of the lead-smelting works at Bagillt, near Holywell, Flintshire, for the drawings from which the annexed woodcuts, figs. 8, 9, 10, have been prepared: *a*, hemispherical pot of cast-iron, having a flange, *b*, *b*, at the top, and another lower down, *c*, *c*, which extends all round except opposite the grate as shown at G fig. 10; *d*, the fire-bars; *e*, *e*, upper part of the fire-place expanded under the bottom of the pot; *f*, *f*, flue space; *g*, flue having its own damper, communicating with a stack common to a row of similar pots; *h*, *h*, hoop of wrought-iron to tie the brickwork together. The line at *f*

on the left of fig. 9 indicates the level of the floor on which the workmen stand; and a similar line on the right near the bottom in the same figure indicates the level of the floor or passage for stoking; at the end opposite the steps this passage should communicate with the exterior of the building for convenience in supplying fuel and removing ashes. It will thus be perceived that this passage is much below the working floor, from which it is reached by steps. There are holes 9″ square, c, c, c, c, communicating with the flue round the bottom of each pot, which are filled up by the potmen, and opened by them from time to time in order to clear out the dust and ashes, which accumulate therein. Each pot must have its own fire-place, and must also have a separate flue and damper, so that the draught under each may be entirely stopped when necessary. Mr. Pattinson

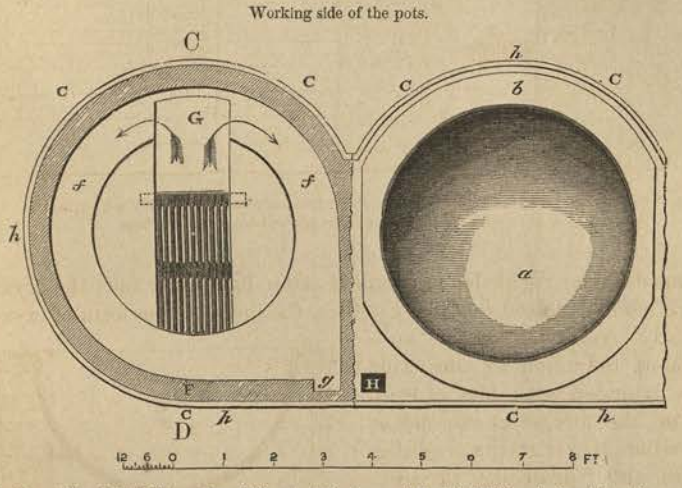


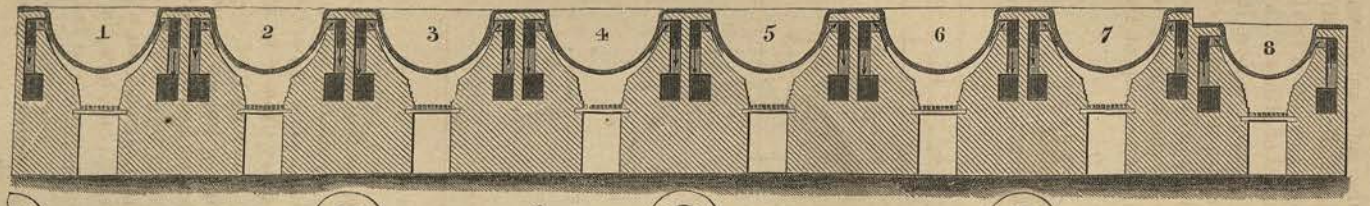
Fig. 10. The right half is a plan of the pot at the top, and the left half is a horizontal section on the line A B, fig. 8.

insisted upon an ash-pit door as well as a fire-door. In his account of his process as it was originally conducted, he says, "above the centre of the line of pots at the height of 6′ or 8′ it is convenient to have a small iron railway with a frame or carriage on four wheels to move backwards and forwards the whole length of the range of pots, from which is to depend a chain, terminated by a hook at the bottom and reaching to nearly the top of the pots, for the purpose of more easily conveying the ladles filled with crystals from pot to pot." A ladle when empty is stated to weigh about 130 lbs., and when full of drained crystals, from 330 to 440 lbs.[2]

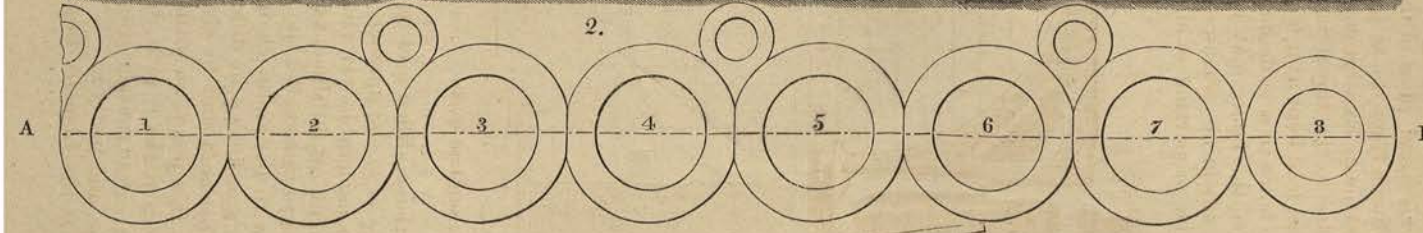
The woodcut on the next page, fig. 11 (1), represents a series of pots in vertical section on the line A B of the plan (2). A vertical section of a pot through the centre at right angles to the line A B (2),

[2] Gruner, Ann. des Mines, 6. sér. 13. p. 383. 1868.

1.

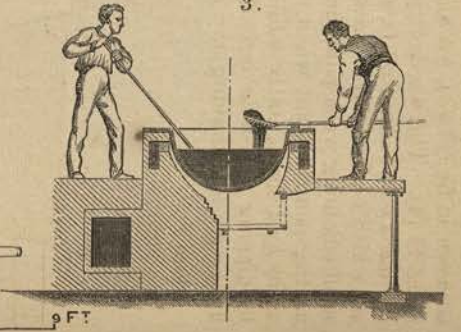


2.



The scale is not given to 1, 2, 3 of this woodcut.

3.



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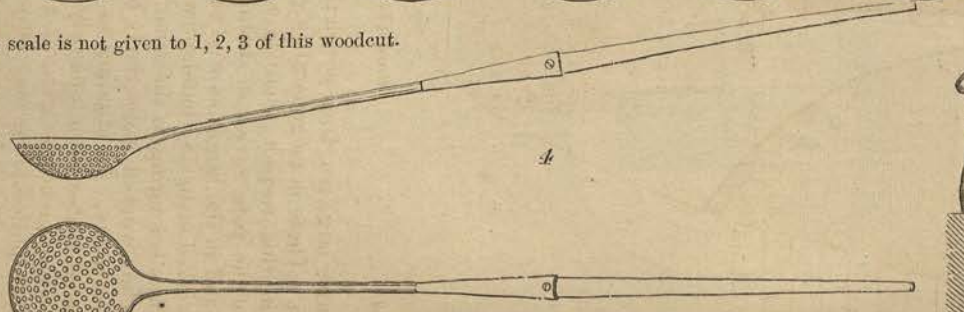

Scale of the ladle.

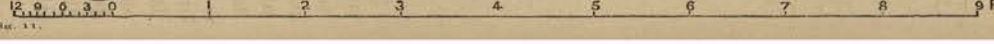

Fig. 11.

is shown in fig. 11 (3). A side view and plan of the ladle are shown in fig. 11 (4). The woodcut is drawn from the actual ladle which Mr. Pattinson sent to the first International Exhibition in London in 1851, and which he afterwards presented to the Royal School of Mines. The small adjoining wash-pots contain lead kept at a temperature *above* its melting-point, so that when the holes in a ladle happen to be stopped up by lead accidentally solidified, the latter may be quickly removed by dipping the ladle into the adjoining wash-pot, which must be filled with lead having the same proportion of silver as that of the

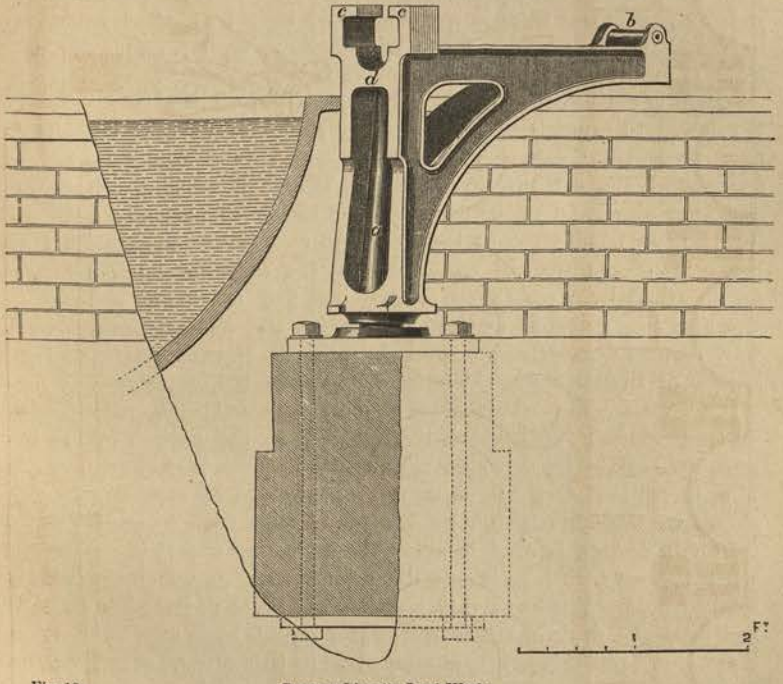

Fig. 12. Crane at Llanelly Lead Works.

adjoining large pot, from which the solidified lead in the ladle has been taken. There is no general rule as to the number of pots in a series; and in this respect there is considerable variation. The capacity also of the pots varies in different establishments, say from 6 to 10 tons, and in the larger as well as in the smaller the ladles may be and are worked either by hand, or with the aid of chains or cranes; and in works belonging to the same proprietors in different localities the ladles are worked respectively by hand and by chains in pots of the same capacity. In alluding to this point, an intimate friend, an experienced lead-smelter, quaintly remarks, "each work considers that its mode of procedure gives it great advantage over any other, a fact at which philosophers may smile, and justly so."

A crane which I saw in use at the Llanelly Lead Works, October,

1869, and for a drawing of which I am indebted to Mr. Charles Nevill, is represented in the woodcut on p. 127, fig. 12. It is made of cast-iron. It revolves round a fixed conical pillar, *a*. At the end of the arm is a roller, *b*, which serves as a fulcrum for the handle of the ladle. After the ladle is immersed in the crystallizing mass of lead, a chain connected with a crab is attached to the handle. By working the crab the handle is pulled downwards and forwards through the opening between, *c c*, so as to rest in the hollow at *d*, and by moving it a little sideways, it is prevented from rising by the projecting pieces, *c c*. There is one such crane opposite the junction of each successive pair of pots. The crab is moveable, and may be shifted where required. The ladles were large and shallow, each holding about 5 cwts. of drained crystals.

Mode of conducting Pattinson's Process.—The molten lead before it is allowed to crystallize is thoroughly skimmed, so that its surface may be quite clean. The fire is withdrawn, the damper put down, and the ash-pit door closed. The lead is thus allowed to cool very slowly, care being taken to break off and mix with the liquid mass from time to time any portion that may congeal on the sides of the pot, in which case if the solidified portion cannot be detached by mechanical means, the fire must be replaced in the grate in order to melt it off. When the temperature descends to a certain degree, small solid particles or crystals begin to form, chiefly at the surface, which, if left undisturbed, would cohere into a solid crust. The whole mass of metal is continually stirred with an iron rod, and the crystals thereby sink to the bottom of the pot and accumulate in considerable quantity. The perforated ladle is now introduced and raised up full of crystals by resting the iron shank on the edge of the pot. A pig of lead with a bar of iron let into it in casting is used to shake the ladle on; and it is convenient when the pot is full, as it acts like a knife-edge on which the ladle is easily jerked. While in this position the ladle is jerked in order to facilitate the draining through of the liquid lead, after which the crystals are put into the adjoining pot. In this process of jerking the crystals seem almost as little adherent to each other and as mobile as grains of sand. In this way the operation is conducted until two-thirds or three-fourths or more of the original lead are crystallized and withdrawn from the pot.[3] The different pots at each stage are always filled up with lead of the same content of silver as that which they respectively contained prior to crystallization; and Mr. Pattinson observes that the practice with respect to the amount of crystals taken out differs at almost every establishment.

The pots being in working order, it requires about an hour to melt the charge of pigs of lead in a pot over a good fire; but as hot crystals have to be melted, and as they melt in one pot whilst the other pot is being worked, this time is not needed. The custom is

[3] The foregoing description is taken chiefly from the paper which Mr. Pattinson communicated to the British Association.

during each shift to work three pots by two men. The shift varies from 6 to 12 hours, 8 hours being a frequent shift. In 12-hour shifts four pots are generally worked, one being an extra pot, and extra payment is made to the workmen. In order to hasten the cooling of the lead, and, consequently, the crystallization, it is customary to throw water on its surface. This practice is in no way prejudicial if stopped when crystals begin to form; and without it 6 or 8-hour shifts would be impossible, as too much time would be needed for cooling.

It is desirable that there should be a permanent record of the mode of conducting this process from the pen of Mr. Pattinson himself, and I therefore publish a description which, with the exception of a few unimportant verbal alterations, is Mr. Pattinson's own, and which he prepared at my request for my use as Lecturer on Metallurgy at the Royal School of Mines.

The following account contains nearly all the information I am even now (Dec. 1855) able to give relative to the process which bears my name. It is possible that some readers may wish to have a detail of the exact manipulation required to separate a given quantity of lead into portions poor and rich in silver. I have never before thought it necessary to give this information, because from the beginning the process has been performed differently at different establishments. I will now, however, give a full and accurate detail of one mode of proceeding, by which this separation can be accomplished very perfectly and without any costly apparatus.

We must be provided with seven crystallizing-pots, each with its heating-pot attached, and one pot for melting the poor lead, called the market-pot. Each crystallizing-pot must be capable of holding, when filled to within five or six inches of the brim, about 6½ tons of melted lead, and the market-pot should hold about 3 tons of lead. The woodcut at p. 126 shows the arrangement of the pots. Let us suppose we have 846 cwts. of lead to separate, containing 7 to 8 ozs. of silver per ton, and that we have in stock besides from previous operations remaining in the different pots as follows:—

		cwts.		ozs.		ozs.	
In Pot No.	1	54	of lead, containing	75	to	80	of silver per ton.
,,	2	54	,,	38	,,	40	,,
,,	3	54	,,	16	,,	18	,,
,,	4	36	,,	7	,,	8	,,
,,	5	36	,,	3½	,,	4½	,,
,,	6	36	,,	2	,,	2¼	,,
,,	7	36	,,	¾	,,	1¼	,,

the market-pot being empty. The small heating and washing-pot must also be full of the same sort of lead as its crystallizing-pot contains; but as this is never used except for heating and washing the ladles, it is unnecessary to consider it further.

Operation 1.—We begin the separation by putting 90 cwts. of the original lead (part of the 846 cwts. we are proceeding to separate)

into pot No. 4. The whole 126 cwts. of lead now in pot No. 4 are melted, skimmed, cooled, and crystallized; and the portion of lead withdrawn by skimming is supplied by lead reduced from other similar skimmings (*i.e.* from the same pot) of previous operations. There are now laded over into No. 5, 90 cwts. of crystals containing $3\frac{1}{2}$ to $4\frac{1}{2}$ ozs. of silver per ton, and the remaining 36 cwts. of enriched lead, which we may call *once* enriched lead, containing about 16 to 18 ozs. of silver per ton, are laded into No. 3, to be afterwards further enriched, leaving No. 4 empty. No. 5, now containing 126 cwts. of 4-oz. lead, is melted, skimmed, cooled, and crystallized,[4] the skimmings being replaced as before: 90 cwts. of crystals, containing 2 to $2\frac{1}{4}$ ozs. of silver per ton, are laded over into No. 6, and 36 cwts. of fluid lead, containing 7 to 8 ozs., go back into No. 4. No. 6 is now treated in the same way, and 90 cwts. of crystals, containing 1 to $1\frac{1}{4}$ oz. of silver per ton are laded over into No. 7, and 36 cwts. of fluid lead, containing about 4 ozs. per ton go back to No. 5. No. 7 is now proceeded with, and from it 54 cwts. of crystals containing from 7 to 10 dwts. of silver per ton are laded over into the market-pot; and here it is to be observed, that if more than this quantity were put into the market-pot the separated lead would be too rich, and some silver consequently wasted; and yet the 72 cwts. still in No. 7 cannot all be laded over into No. 6. To avoid this, a mode of proceeding now is to lade out of No. 7 a further quantity of crystals, say 36 cwts., and to lay them down on the floor: these may be called intermediate crystals, and will contain about 1 or $1\frac{1}{4}$ oz. of silver per ton. The remaining 36 cwts. of fluid lead, containing about $2\frac{1}{4}$ ozs. per ton, are laded over into No. 6, and then the 36 cwts. of intermediate crystals are put back from this floor into No. 7, and so the first operation is completed. It will be seen that by this operation the 90 cwts. of original lead added to No. 4 have been divided by four crystallizations into 54 cwts. of poor lead in the market-pot, and 36 cwts. of *once* enriched carried to No. 3. All the other pots remain as they were at first.

Operation 2.—This is begun by putting again 90 cwts. of original lead into No. 4, from which 36 cwts. of lead once enriched are carried to No. 3, the poor lead passing through Nos. 5, 6, and 7 as before, until 54 cwts. of poor lead are again supplied to the market-pot, leaving the rest of the pots as they were at first except No. 3, which now contains its original stock of 54 cwts. of lead once enriched and 72 cwts. of the same lead added from the two operations, making altogether 126 cwts. This pot, being now full, is crystallized, and 72 cwts. of crystals, containing from 7 to 8 ozs. of silver per ton, are laded into No. 4: 18 cwts. of intermediate crystals, containing from 14 to 18 ozs., are laid down upon the floor to be afterwards put back into the same pot; and 36 cwts. of *twice* enriched lead, containing

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[4] The technical expression here used of *crystallizing a pot* will be understood to refer to the contents of the pot.

from 38 to 40 ozs. of silver per ton, are laded into No. 2, and the 18 cwts. of intermediate crystals are returned to No. 3.[5]

At the end of this operation the state of the pots is as follows :—

Pots	1	2	3	4	5	6	7
Cwts.	54	90	18	108	36	36	36

and 108 cwts. of poor lead have been made into the market lot.

Operation 3.—This is begun by adding 18 cwts. of original lead to No. 4, after which Nos. 4, 5, 6, and 7 are crystallized, producing 54 cwts. of poor lead to the market-pot and 36 cwts. of *once* enriched lead to No. 4. The state of the pots now is :—

Pots	1	2	3	4	5	6	7
Cwts.	54	90	54	36	36	36	36

Operation 4.—90 cwts. of original lead are added to No. 4, which with Nos. 5, 6 and 7, is crystallized, yielding 36 cwts. of once enriched lead to No. 3, and 54 cwts. of poor lead to the market-pot. The state of the pots is as follows :—

Pots	1	2	3	4	5	6	7
Cwts.	54	90	90	36	36	36	36

Operation 5.—This is just the same as the last :—36 cwts. of once enriched lead have passed to No. 3, and 54 cwts. of poor lead to the market-pot. The state of the pots is as follows :—

Pots	1	2	3	4	5	6	7
Cwts.	54	90	126	36	36	36	36

Operation 6.—No. 3 being now full, it is crystallized, yielding 36 cwts. of twice enriched lead to No. 2, and 72 cwts. of lead similar in content of silver to the original lead to No. 4. After this the state of the pots is as follows :—

Pots	1	2	3	4	5	6	7
Cwts.	54	126	18	108	36	36	36

This operation is now continued by adding 18 cwts. of original lead to No. 4, which, with Nos. 5, 6 and 7, is crystallized, yielding 36 cwts. of once enriched lead to No. 3, and 54 cwts. of poor lead to the market-pot. But No. 2 being now full, it is crystallized, by which 36 cwts. of thrice enriched lead are passed to No. 1, and 72 cwts. of twice enriched lead to No. 3. After this the state of the pots is as follows :—

Pots	1	2	3	4	5	6	7
Cwts.	90	18	126	36	36	36	36

Operation 7.—No. 3 is crystallized, yielding 36 cwts. of twice enriched lead to No. 2, and 72 cwts. of original lead to No. 4. This pot is filled up with 18 cwts. of original lead and crystallized, as are also

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[5] Dick informs me that he has never seen intermediate crystals taken out at so low a produce; and he does not think it is now practised until the concentration has been carried much further, say at 8th or 9th pot.

Nos. 5, 6 and 7, 36 cwts. of once enriched lead passing to No. 3, and 54 cwts. of poor lead to the market-pot. The state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	90	54	54	36	36	36	36

Operation 8.—90 cwts. of original lead are added to No. 4, which is crystallized as before, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of once enriched lead to No. 3.

Operation 9.—90 cwts. of original lead are added to No. 4, which is crystallized, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of once enriched lead to No. 3. The state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	90	54	126	36	36	36	36

Operation 10.—18 cwts. of original lead are added to No. 4, and Nos. 3, 4, 5, 6 and 7 are crystallized, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of twice enriched lead No. 2. The state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	90	90	54	36	36	36	36

Operation 11.—90 cwts. of original lead are added to No. 4, which is crystallized, as are also Nos. 5, 6 and 7, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of once enriched lead to No. 3.

Operation 12.—This is precisely the same as the last, after which the state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	90	90	126	36	36	36	36

Operation 13.—18 cwts. of original lead are added to No. 4, and Nos. 3, 4, 5, 6 and 7 are crystallized, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of twice enriched lead to No. 2. After this the state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	90	126	54	36	36	36	36

Operation 14.—18 cwts. of original lead are added to No. 4, and Nos. 2, 3, 4, 5, 6 and 7 are crystallized, 54 cwts. of poor lead passing to the market-pot, and 36 cwts. of thrice enriched lead into No. 1. The state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	126	54	54	36	36	36	36

Operation 15.—18 cwts. of original lead are added to No. 4, and all the pots are crystallized, after which 36 cwts. of 4-times enriched lead, containing about 160 to 170 ozs. of silver per ton, will be found

in No. 1, and 54 cwts. of poor lead will pass to the market-pot. The state of the pots is as follows:—

Pots	1	2	3	4	5	6	7
Cwts.	54	54	54	36	36	36	36

which is exactly the same as that at the beginning of the operations.

The results of the whole series of operations may be stated as follows:—

	Original lead added.	Poor lead produced.
Operation 1	..... 90 cwts.	..... 54 cwts.
,, 2	..... 90 ,,	..... 54 ,,
,, 3	..... 18 ,,	..... 54 ,,
,, 4	..... 90 ,,	..... 54 ,,
,, 5	..... 90 ,,	..... 54 ,,
,, 6	..... 18 ,,	..... 54 ,,
,, 7	..... 18 ,,	..... 54 ,,
,, 8	..... 90 ,,	..... 54 ,,
,, 9	..... 90 ,,	..... 54 ,,
,, 10	..... 18 ,,	..... 54 ,,
,, 11	..... 90 ,,	..... 54 ,,
,, 12	..... 90 ,,	..... 54 ,,
,, 13	..... 18 ,,	..... 54 ,,
,, 14	..... 18 ,,	..... 54 ,,
,, 15	..... 18 ,,	..... 54 ,,
Total	 846	 810
	Rich lead obtained	36 cwts.
		846 cwts.

We have thus divided the 846 cwts. of original lead operated upon into

36 cwts. of rich lead, containing from 160 to 170 ozs. of silver per ton,
and 810 cwts. of poor lead, containing from 7 to 10 dwts. ,, ,,
Ratio between enriched and poor lead is 1 : 22·5.

It is obvious that this rich lead may be further enriched, and the enrichment is generally carried to the degree of from 200 to 300 ozs. per ton, which limit it is not often thought profitable to exceed.

The quantity of silver contained in the lead of all the different crystallizations is stated always with some license, which it is impossible to avoid, as in this respect the lead varies continually. Some lead crystallizes much better than other lead, from being purer. Besides, the workmen are not always exact in the quantity they take out of each pot; and perhaps the quantity of crystals existing in the pot from which they are lading may be greater or less, as the holes in the ladles may be more or less open and clean, all of which circumstances cause the process somewhat to vary. The variation is not, however, to any great extent, and does not affect the general result of the operation, provided care is always taken to deprive the poor lead almost entirely of its silver.

In the mode of performing the process just described, the original lead is assumed to contain from 7 to 8 ozs. of silver per ton, and this can be sufficiently deprived of its silver by four crystallizations. Should it, however, hold from 10 to 12 ozs. of silver per ton, five or

six crystallizations will be required; and if it contain only from 5 to 6 ozs. per ton, the market-lead may be made poor enough by three crystallizations.

The law is so evident that further description is unnecessary.

H. L. PATTINSON.

Scots House, Newcastle on Tyne, 31st Dec., 1855.

The weight of lead lifted, say about 2 ft., in the foregoing fifteen operations, is as follows :—

	Cwts.		Cwts.
No. I.	630	No. IX.	630
„ II.	774	„ X.	702
„ III.	558	„ XI.	630
„ IV.	630	„ XII.	930
„ V.	630	„ XIII.	702
„ VI.	846	„ XIV.	846
„ VII.	702	„ XV.	990
„ VIII.	630		

Total = 10,530 cwts. = 526 tons 10 cwts. = 2,358,720 lbs. raised 1′ high.

Modifications in the mode of conducting Pattinson's process.—No rigid and definite general rule can be laid down as to the course of proceeding, which may be varied according to the particular requirements at the lead works. The process, however, is now usually conducted according to two schemes, one called the method by *thirds*, and the other the method by *eighths*. In the first of these schemes the lead in each pot is divided by crystallization into two portions, namely, $\frac{2}{3}$ of crystals and $\frac{1}{3}$ of fluid lead. In the other scheme it is divided into $\frac{7}{8}$ of crystals and $\frac{1}{8}$ of fluid lead. It will be perceived that the process above described by Mr. Pattinson approximates closely to the first scheme, the proportions of crystals and fluid lead being, respectively, $\frac{5}{7}$ and $\frac{2}{7}$, instead of $\frac{2}{3}$ and $\frac{1}{3}$; or, as it may be otherwise stated, $\frac{4}{6}$ and $\frac{2}{6}$. A graphic representation of this method, which may be regarded as only a modification of the method by *thirds*, is presented in the annexed diagram.

It will be asked, why there should be so much variation in the mode of conducting Pattinson's process at different establishments, British as well as foreign, and whether, in the desilverization of the same kind of lead, there is not one method which gives a more profitable result than any other? I am not in possession of sufficiently accurate data to enable me to answer those questions in a satisfactory manner. In some cases, it can hardly be doubted, the method adopted has been capriciously and arbitrarily selected. It is, however, maintained, that the method of thirds is most applicable to rich, and that of eighths to poor, argentiferous lead. The same lead may be treated by a combination of both of those methods; thus, the process may be begun by the method of thirds, and completed by that of eighths; and, conversely, the treatment of poor argentiferous lead may be begun by the method of eighths, and the resulting enriched lead be treated by the method of thirds.[6]

[6] Gruner, Ann. des Mines, 6 sér. 13, p. 382, 1868.

[*To face page* 135.

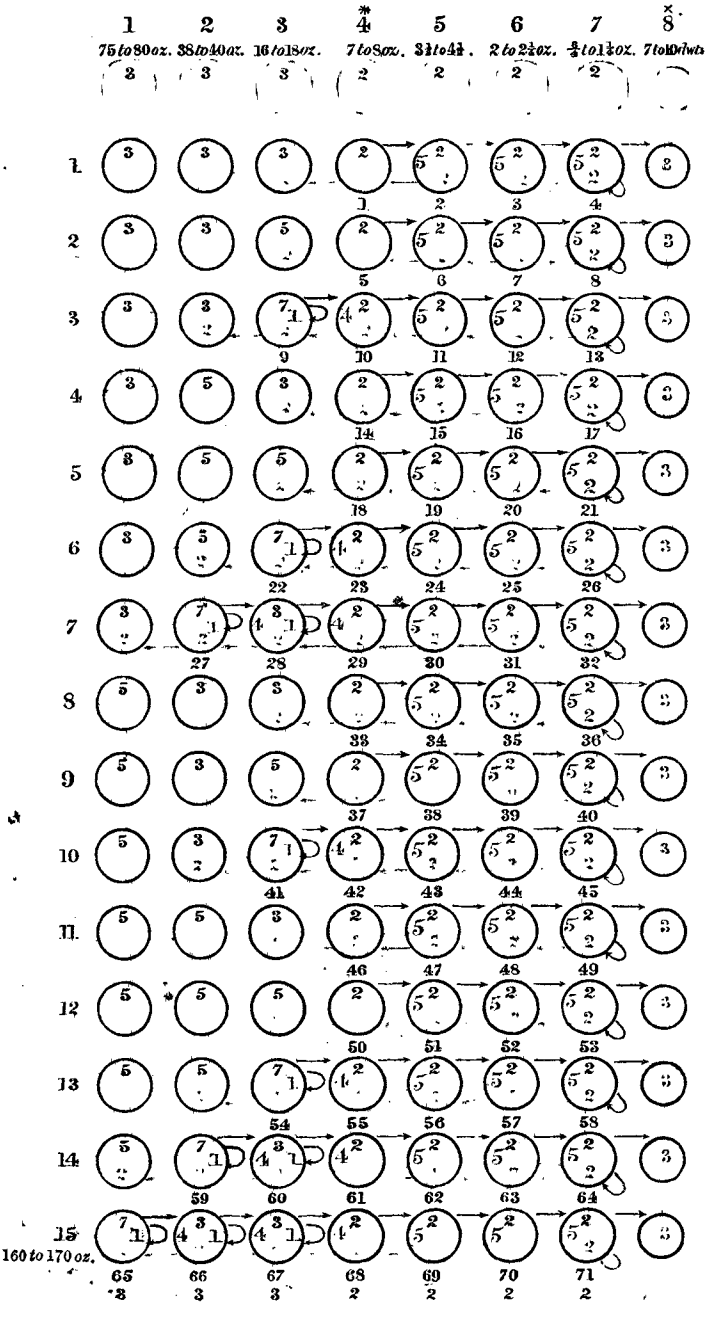

DIAGRAM OF PATTINSON'S PROCESS.

Description of the annexed diagram.—The *circles* represent the *pots*, which are numbered 1, 2, 3, 4, 5, 6, 7, and 8, respectively; and the signs * and × indicate the *centre* and *market* pots respectively. The *black* figures *within* the circles indicate the state of the pots at the commencement of each of the 15 series of crystallizings. The figures *within* the *blue* circles show the state of the pots *before* and *after* the operation. The *black* figures from 1 to 71 *under* the circles indicate the consecutive order of the crystallizings. The *yellow* figures indicate the *original lead* operated on; the *red* figures, the *crystals* of lead removed at each crystallizing; the *red straight arrows*, the pots to which the crystals are transferred; the *curved red arrows* that the *intermediate crystals* are taken out and returned to the same pot after the liquid lead has been removed; the *blue* figures, the *liquid enriched lead:* and the *blue arrows*, the pot to which it is transferred. Thus, by way of example, pot 4 contains 2 parts of lead (black figures), to which are added 5 parts of original lead (yellow figures); this lead is now crystallized (1), when 5 parts of crystals (red figures) are passed into pot 5, and two parts of liquid enriched lead (blue figures) into pot 3.

In order further to elucidate the scheme shown in the table, the following statement and remarks are presented. The quantities operated upon, according to that scheme, are in every instance multiples of 18:—

126 cwts.	=	18	×	7	.....	or $\frac{7}{7}$ths.
108 „	=	18	×	6	.....	or $\frac{6}{7}$ „
90 „	=	18	×	5	.....	or $\frac{5}{7}$ „
72 „	=	18	×	4	.....	or $\frac{4}{7}$ „
54 „	=	18	×	3	.....	or $\frac{3}{7}$ „
36 „	=	18	×	2	.....	or $\frac{2}{7}$ „
18 „	=	18	×	1	.....	or $\frac{1}{7}$ „

7 or $\frac{7}{7}$ths represent the quantity in each pot when full and ready for crystallizing. The original lead is added in constant quantities of $\frac{1}{7}$th and $\frac{5}{7}$ths, and the $\frac{7}{7}$ths in each pot are divided on crystallizing into $\frac{5}{7}$ths of crystals and $\frac{2}{7}$ths of enriched lead. On examination of the table, it will be found that the $\frac{47}{7}$ths of *original lead*, added in 15 portions of $\frac{1}{7}$th, or $\frac{5}{7}$ths, are by 71 crystallizings separated into 15 times $\frac{3}{7}$ths or $\frac{45}{7}$ths of *market-lead* and $\frac{2}{7}$ths of *enriched lead*. With regard to the silver, if $\frac{1}{7}$th represents one ton of lead, then it will be seen that 47 tons of original lead, containing $7\frac{1}{2}$ ozs. of silver per ton, have been separated into 45 tons of market-lead, containing $\frac{1}{2}$ oz. of silver per ton, and 2 tons of enriched lead containing 165 ozs. of silver per ton. Thus—

Original lead	$7\frac{1}{2}$ ozs.	× 47	=	$352\frac{1}{2}$ ozs.
Market-lead.....	$\frac{1}{2}$ oz.	× 45	=	$22\frac{1}{2}$ ozs.
Enriched lead.....	165 ozs.	× 2	=	330 ozs.
				$352\frac{1}{2}$

The loss of silver in the market-lead is 6·384% of the total amount

of silver contained in the original lead, and the enriched lead contains 93·616% of the total amount contained in that lead.

Observations on Pattinson's Process.

The expression commonly used of "desilverized" by this process is correct only when restricted to the impoverished or market-lead.

One fact of great practical importance in this process is, that other metals besides silver, which may be present in the lead, are to a certain extent concentrated in the enriched portion; or, in other words, to cite the illustration of Mr. Pattinson, the lead separated by crystallization is in a greater or less degree freed from metallic impurities, just as water in freezing is freed from saline matters, which may have been dissolved in it. By such purification the malleability, ductility, and softness of the lead are increased. But Mr. Pattinson considered that the separation of foreign metals from the lead was due not wholly to crystallization, but in part to the oxidation of those metals. Thus, he writes "when the crystals are withdrawn from the liquid lead, being in the state of a coarse and very clear metallic powder, they are most readily acted upon by the oxygen of the atmosphere, which penetrates everywhere among them, and comes in contact with a great extent of heated surface, the more oxidizable metals, as iron, zinc, etc., contained in the lead and giving it hardness are seized upon and converted into oxides, which, when the crystals are re-melted, separate as dross. It is not improbable that the crystals are somewhat in the condition of Döbereiner's spongy platina or Faraday's clean metallic plates, by which the air is drawn into the most intimate contact with them, and made even to undergo some degree of condensation in their interstices, by which its action is rendered more energetic." That oxidation in the manner described would tend to remove such metals as iron and zinc, there is no reason to doubt; but that this explanation of the purification of lead by Pattinson's process is, to say the least, only partial, is established by the fact that concentration of certain foreign metals in the residual liquid lead has been proved by direct chemical analysis.

As the melting-point of silver is much higher than that of lead, it might be supposed, that the portion of the lead first solidified would contain more silver than the other portion; and on this ground Mr. Pattinson remarks that his process "is certainly somewhat paradoxical." It has been demonstrated that several, not to say many, alloys melt at lower temperatures than those of their ingredients which have the lowest melting-points. Various so-called fusible metals may be adduced in illustration of this statement. But that there is a difference, though extremely small, between the melting-points of lead comparatively free from silver and lead alloyed with silver in certain proportions, is shown by the result of Mr. Pattinson's experiment on the draining of lead crystals previously recorded. Notwithstanding the fact that "if the draining is carried far enough, the lead left behind is entirely deprived of silver," yet the difference of fusibility just mentioned "is by no means sufficient

to allow of the separation of silver from lead by the ordinary process of eliquation," as is demonstrated by the following experiments of Mr. Pattinson. "Pieces (*i.e.* pigs or ingots) of lead were exposed for hours upon an iron grating in the chamber of a large reverberatory furnace to a heat most cautiously increased, until a few drops of fused metal oozed out from their pores; this was found to be but slightly, although decidedly, enriched. In one of the most carefully conducted experiments, a piece of lead containing silver to the extent of 5 ozs. 0 dwt. 8 grs. per ton yielded drops containing 7 ozs. 7 dwts. 9 grs., and when drained to one-third of the original quantity, the portion left still held silver in the proportion of 3 ozs. 13 dwts. 16 grs. per ton. In another experiment a piece of the same lead, drained most slowly to one-fourth or one-fifth of the original quantity, left residual lead containing silver to the extent of 1 oz. 17 dwts. 15 grs. per ton. In these experiments," Mr. Pattinson concludes, "as in the draining of the crystals, the separation is effected by the difference of fusibility between pure lead and lead containing silver, aided no doubt by the tendency of pure lead in that state of semifluidity to assume a crystalline form."

Now, it would appear from the foregoing data, that lead alloyed with silver in some proportions melts at a lower temperature than pure lead; but it is also certain that the reverse is the fact in the case of lead alloyed with silver in other proportions; as, for example, in that of silver alloyed with a comparatively small quantity of lead, say even three times its own weight. Hence, it might with reasonable confidence be predicted that the concentration of silver by Pattinson's process would not proceed beyond a certain degree; and the truth of that prediction has been confirmed by experiment. We are indebted to C. Reich for the following precise and conclusive investigation on this subject, which was conducted at the Halsbrücke works in Freiberg.[7] It may be stated as established that the richer the lead is in silver, the smaller and more difficult to drain are the crystals.

Silver per cent.		
In the molten lead before crystallization.	In the laded-out lead.	In the residual lead or "mother-liquor."
0·704	0·390 to 0·466	1·025
0·732	0·318 ,, 0·374	1·076
0·966	0·410 ,, 0·680	1·450
0·988	0·390 ,, 0·624	1·530
1·442	0·682	1·922
2·090	2·011	2·260
2·116	1·728 ,, 2·216	2·248
2·206	2·212	2·264

"When the concentration of the silver had reached the degree of about $2\frac{1}{4}\%$ of the lead, the formation of crystals of lead proceeded

[7] Wagner's Jahresbericht, 1862, p. 174.

far more slowly than with a lower proportion of silver; and at the commencement the tendency of the whole mass of liquid lead to solidify was unmistakeable. It was only after much trouble, by carefully and repeatedly detaching the solidified metal from the sides of the pot, and by constant stirring, that crystals could be laded out."

By operating upon lead containing 2·266% of silver Reich got the following results: By the usual manipulation in Pattinson's process,

The small crystals contained of silver per cent.	2·188
The large do. do. do.	2·337
Mean	2·2625

By very careful, strong shaking of the ladle so as to detach as far as possible the adherent mother-liquor,

The small crystals contained of silver per cent.	2·246
The large do. do. do.	2·348
Mean	2·297

At the end of this process of over-crystallization by the usual manipulation,

The small crystals contained of silver per cent.	2·304
And by very careful shaking do.	2·300

The whole of the crystals separated were melted together and the resulting lead contained 2·264% of silver, while the mother-liquor or residual lead contained 2·292% of silver. The difference is so small that practically it may be disregarded; and the conclusion is that concentration of silver in lead by Pattinson's process cannot be carried further than $2\frac{1}{4} = 2{\cdot}25\%$ of the lead. Mr. Dick informs me that he had from large experiments deduced 700 ozs. of silver per ton of lead as about the extreme limit of enrichment, *i.e.* 2·14%, which is very nearly the limit assigned by Reich.

Stetefeldt, a German metallurgist, has exercised his ingenuity in the mathematical treatment of Pattinson's process; but, so far as I can judge, he does not seem to have arrived at any result of practical value.[8]

Effect of foreign metals upon Pattinson's process.—The effect of small quantities of antimony, arsenic, and copper in lead is to make the crystals smaller, just as silver does; and more time is required to drain small crystals than large, and the period of drainage being thus protracted, the richer liquid lead sets in part on the surface of each crystal and so is carried over into the poorer pot.

Proportion of skimmings and loss of lead.—This *cæteris paribus* depends on the proportion of silver, and consequent number of crystallizations. Lead containing 8 ozs. of silver per ton will yield from first to last during Pattinsonization about 20% of skimmings. These skimmings consist for the most part of oxidized lead, and are subjected to the same kind of reducing process as litharge, of which a description will

[8] Berg- u. hüttenm. Zeitung, 1863, pp. 64, 69-77.

be given in the sequel. The total loss of lead in the process may be estimated at about 12 or 14 lbs. per ton; but this will also vary with the quality of the lead operated upon.

Time and labour required in Pattinson's process.—In general two men work together, and crystallize three pots holding about 12 tons in 12 hours.[9] At Tarnowitz three men work together during 8-hour shifts; and a pot holding about 15 tons is skimmed, crystallized, and its contents laded into the two adjoining pots in $2\frac{1}{4}$ hours.[10]

Cost of Pattinson's process.—Mr. Pattinson estimated the total cost at 3 ozs. of silver per ton of lead, *i.e.* at about 15*s.*, inclusive of the loss of lead and all expenses of desilverizing and refining; and precisely the same estimate was communicated to me in 1850 by the late Mr. John Taylor, so long and honourably known in connection with British and foreign mining. As far as I have been able to ascertain, the cost in this country, as well as on the continent, is generally between 2 and 3 ozs. of silver per ton, *i.e.* between 10*s.* and 15*s.* The proportion of silver in the lead will obviously determine the number of crystallizings, and, consequently, affect the cost of the process. Fuel and labour must always be variable items in different localities; but the quality of the lead treated is not without influence on the cost, for when inferior on account of the presence of certain foreign metals, the process is conducted less easily and more slowly than in the case of comparatively pure lead. It may be laid down as a general rule that the purer the lead, the better is it adapted for Pattinson's method of desilverization. The cost of the labour in Pattinsonizing 1 ton (*i.e.* 1000 kilogrammes) of lead is at Freiberg, 4*s.* 5·3*d.*, in Belgium and at Stolberg, from 4*s.* 3·7*d.* to 4*s.* 8·4*d.*, and at Tarnowitz, 5*s.* 10·5*d.*; and the total costs at those localities per ton are 10*s.* 7*d.*, 9*s.* 6·6*d.*, and 12*s.* 9*d.*, respectively.[11]

The question has been put why, if lead as it comes from the furnace in pigs containing $1\frac{1}{2}$ oz. of silver per ton cannot be profitably desilverized, should the impoverishment of the lead in Pattinson's process be carried so low as $\frac{1}{2}$ or $\frac{3}{4}$ oz. per ton? The answer of an experienced lead-smelter is, that furnace-lead would require conveying to the pot, melting, skimming, and lading out, which would cause a charge in addition to that attending the further treatment of lead of like content of silver, obtained in the course of desilverizing originally richer lead, amounting to more than the value of an ounce of silver. Although the managers of lead works must naturally be anxious to show as large a production of silver as possible, yet they should be extremely cautious in considering such a question as that just propounded.

Wrought-iron Pattinson pots.—Cast-iron pots are liable to let lead escape, from cracking or otherwise; and with a view to prevent this evil, pots of welded wrought-iron have been recently introduced into the Tarnowitz Lead Works, with, it is stated, satisfactory results.

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[9] Gruner, Ann. des Mines, 6 sér. 13, p. 383, 1868.

[10] Teichmann, Zeitschrift für das Berg-, Hütten- und Salinenwesen im Preuss. Staate, xv. 1, 1867.

[11] Gruner, op. cit. p. 384.

These pots are 1″ thick, and hold 300 centners, *i.e.* about 15 tons. It is further stated that, although they cost 2½ more than cast-iron pots of the same capacity, yet they last much longer and continue sound, and are really more economical.[12]

Application of Machinery to Pattinson's Process.

In 1860 a patent was granted to Mr. Philip John Worsley for "Improvements in the Separation of Silver and Lead,"[1] which had for their object the substitution of machinery worked by steam or water-power for hand labour in Pattinson's process. The patentee prefers to use crystallizing-pots similar to those used in the ordinary process, but about 2″ above the bottom of the inside of the pot to have a hole drilled through the pot nearly horizontally. This hole may be from a ¼″ to ½″ in diameter, and over it is fastened a strainer of sheet-iron pierced with holes, which should be not more than $\frac{1}{16}$″ in diameter, but as close together as is consistent with the strength of the iron. The strainer is cup-shaped, with a flange round the edge, having no holes in it. The flange must fit close to the pot, and be fastened down by a flat ring of iron exactly covering it, through which screws are driven into the pot. The size of the strainer is from 6″ to 8″ in diameter, and the hollow of the inside about 1″ deep. The second strainer which is over the first is of stouter iron and pierced with ¼″ holes. With this no ring is necessary, the flange of the outer strainer being sufficient to take the screws. This second strainer in some cases is not employed. Underneath the hole in the crystallizing-pot is a spout or channel to carry off the lead as it runs out into another pot placed to receive it; this spout is set in an opening made through the side-wall of the fire-hole of the crystallizing-pot, and the hole in this pot must be so pierced that the lead shall run out directly into the spout. To stop the hole in the crystallizing-pot a "tapping-bar" is used, *i.e.* a bar of iron slightly tapered at the end which is to stop the hole, and of such size as just to fill it. This bar is driven gently into the hole and fixed by a blow from a hammer; it may also be fastened in by a screw to prevent its being knocked out accidentally. To begin the separation the tapping-bar is fixed in the hole so as to stop it, and the argentiferous lead is then melted down; when melted it is cooled with constant stirring as in the ordinary process, but the stirring and cooling are continued much longer than in that process. The stirring should be continued so long as the stirrer can be got through the crystals, if the least possible quantity of liquid lead is wanted to be drawn off, but the length of time during which the stirring must be continued depends upon the quantity of crystals wanted. As soon as the desired quantity of crystals is formed, which is known by the thickness of the mixture of liquid lead and crystals, the tapping bar is withdrawn, and the rich liquid lead run off, the crystals being

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[12] Teichmann, op. cit.

[1] A.D. 1860. Jan. 4. No. 26.

allowed to drain as long as any liquid lead runs from them. The liquid rich lead being all run off, the tapping-bar is replaced, the crystals of poor lead re-melted, and the operation repeated as desired. In case the hole be stopped up with crystals or cold lead, a red-hot bar of iron is had recourse to, which melts the lead closing the hole and lets the liquid enriched lead escape. Or instead a small quantity of hot coals or burning wood may be put round the spout. By this process the rich lead is obtained in the lower pot, while the crystals of poor lead are left in the original crystallizing-pot. Instead of stirring by hand with a slice as is usually done, a mechanical stirrer is employed, consisting of an upright shaft connected with a steam-engine, water-wheel, or other source of power. This shaft is fixed in the centre of the crystallizing-pot, with a bearing at the top and bottom, and carries arms radiating from it extending to the sides of the crystallizing-pot. The shape and number of these arms is not very material, but flat arms with a thin edge foremost are preferred and inclined so that the front edge is lower than the back. This invention was carried into practice at Rotherhithe, but from causes presently

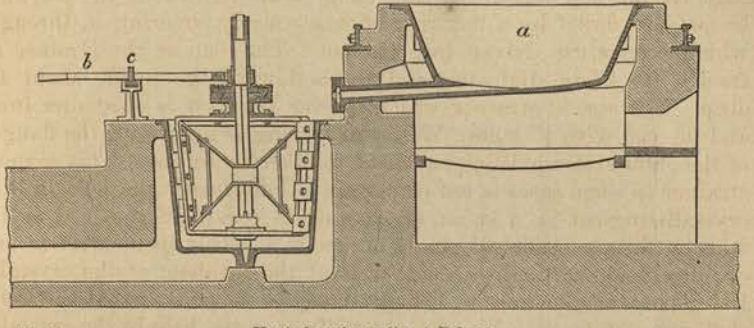

Fig. 13. Vertical section on line A B fig. 15.

to be stated it was not long afterwards abandoned. Mr. T. B. Jordan, an ingenious mechanical engineer, well known by his machinery for wood-carving, was employed to design and construct the machinery for this process, and to him I applied for information on the subject as well as for illustrative drawings, an application to which he promptly responded by presenting me with both. The annexed woodcuts have been executed after those drawings, and the following description is, with few unimportant exceptions, Mr. Jordan's own.

The melting and crystallizing are conducted, not as usual in Pattinson's process in the same pot, but in two pots, which will henceforth be designated the *melting* and *crystallizing* pots.

The entire process of desilverization may be effected in this one set of two pots, but several sets would be needed in large works. The melting-pot, *a*, is charged with about 12 tons of lead, and kept at a *much higher* temperature than the melting-point of lead. When the proper degree of heat is attained, a portion of the molten lead is drawn off into the crystallizing-pot, the temperature of which is

maintained at a *little above* the melting-point of lead. The stirring frame and scrapers are then brought into action by putting the con-

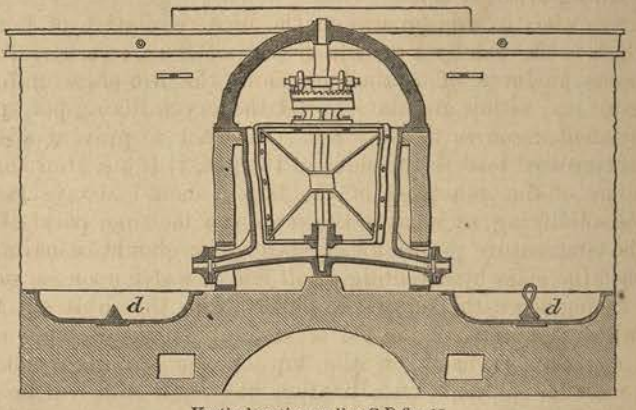

Fig. 14. Vertical section on line C D fig. 15.

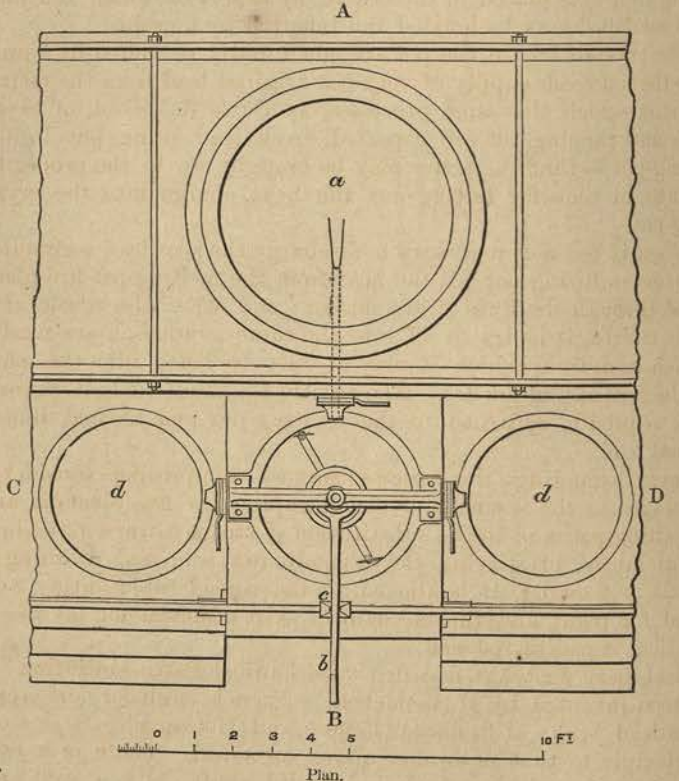

Fig. 15. Plan.

necting lever *b*, into the jaws of the cam on the horizontal rod, *c*, which is kept reciprocating by steam-power; its forward motion is

communicated to the stirring frame by the detents acting on the crown wheel, while it is at rest during the back stroke by the detents falling over the cogs.

Much depends in this process on the nice regulation of temperature, which is effected by a double system of flues, so contrived that the gaseous products of combustion from the fire-place under the melting-pot may either circulate round the crystallizing-pot, or pass away by another course to the stack. In order to prevent adhesion of the crystallized lead to the sides of the pot, it is essential that the temperature of the substance of the latter should always be kept above the solidifying, or what is the same the melting, point of lead, while the temperature proper for crystallization should be maintained in the metallic mass by directing small jets of water upon its surface, and by forcing down the surface so chilled into the subjacent liquid metal, which is done with the aid of an inclined paddle (not shown in the engravings) fixed on the top of the stirring frame and moving with it. When crystallization has made sufficient progress, the enriched liquid lead is drawn off into the ingot-moulds, *d d*, having iron eyes placed in the centre, by means of which the ingots when solidified may be hoisted and removed by a crane.

The crystals left in the pot are now rapidly re-melted by running on to them a fresh supply of very hot original lead from the melting-pot, after which the same processes, as above described, of crystallizing and tapping off are repeated, fresh lead being put into the melting-pot so that the latter may be brought up to the proper temperature in time for letting out the next charge into the crystallizing-pot.

When it becomes necessary to discharge the poor lead accumulated in the crystallizing-pot, all the heat from the melting-pot fire-place is turned through the flues of the former; and when the whole of the lead is melted, it is drawn off into the same moulds as are used for the rich lead, from which it may at once be laded into the market moulds, or reserved for use. The enriched lead of the first process is, when requisite, returned to the melting-pot and treated like the original lead.

Notwithstanding the process seemed to promise considerable advantages in the saving of fuel by keeping the fire constant under the melting-pot, and in the substitution of steam-power for the heavy manual labour of stirring the crystallizing lead and draining the crystals, yet owing, it is alleged, to the considerable outlay necessitated for plant and the mechanical skill essential for its effective operation, it was abandoned.

Machinery for what is called "mechanical Pattinsonization" has also been invented by M. Boudehen, a French engineer, and applied at the lead works of Stolberg, Rouen, and Holzappel. It is similar in principle to that of Jordan above described. There is a hollow vertical shaft, within which is a solid shaft. By a well-known arrangement of bevil-wheels, these shafts are made to revolve in opposite directions. On the lower part of the outer shaft, within the

pot, is fixed a stirrup-like frame, from the sides of which project short flat-edged scrapers. On the inner shaft are fixed flat arms of equal length, arranged spirally, and with their sides oblique. Engine-power of 5 or 6 horses is required to drive this machinery. It is asserted that the cost of manual labour is only half of that in Pattinson's process; and the total saving is estimated at 20 francs (16*s.*) per ton.[2]

Elimination of certain Metals from Lead by Crystallization.

Although it had long been well known to persons engaged in the desilverization of lead by Pattinson's process that, during the concentration of silver, various other metallic impurities in the lead become concentrated with the silver, or are thrown out in the skimmings, partly in the state of oxides, and partly as alloys or compounds, often no doubt of complex constitution, in which sulphur, arsenic and antimony play important parts; yet Baker, if I mistake not, was the first systematically to investigate the subject. The following record of Baker's results has been communicated to me for publication by himself. It is proper to add that this subject has been also investigated by other persons of much skill and experience, who do not wholly agree with Baker in his conclusions. And this will not appear surprising when we consider the extraordinary effect which the presence even of a *minute quantity* of one metal may exert on a very large quantity of another metal. Absolutely pure lead has probably never been seen; and all the lead which has been made the subject of investigation has certainly been more or less contaminated by substances which, though in excessively minute proportion, suffice to cause variation in the results within considerable limits.

Copper.—Baker has particularly investigated the question of the separation of copper from lead by crystallization of the latter. He found that two samples of lead containing 0·0411% and 0·0774% of copper yielded, respectively, the first after seven and the second after six crystallizations, 0·0239% and 0·0642% of copper. Concentration of copper, therefore, in a slight degree takes place in the residual lead, or, as it is termed, enriched lead. On the other hand, he found that when the proportion of copper in lead does not exceed 0·025% a more marked concentration is effected by one crystallization.

Nickel.—Baker has ascertained that when nickel is present in lead in such small proportions as 0·0023% and 0·0057%, it is eliminated in a certain degree by concentration and not by oxidation; for, in operating upon lead containing nickel in the proportions above mentioned, the latter metal was found in the liquid residual lead in the proportions of 0·0043% and 0·0072%. The following experimental results have been obtained by him and published[3]:—

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[2] Gruner. Ann. d. Mines, 6. sér. 13, p. 387. 1868.

[3] Journ. of the Chem. Society. The paper is very short and is given entire, except with a few verbal alterations.

It is well known that, for certain manufactures, lead of a high degree of purity is required. The presence of a very small amount of copper is especially injurious for making white-lead and glass-makers' red-lead. Investigating the cause of a peculiar tint in glass, which was sometimes sufficiently marked to be called blue, and was readily accounted for by the presence of copper, he sought carefully for cobalt, but only found nickel. In all the samples of English lead which he has examined he has never detected a trace of cobalt. On the contrary, traces of nickel have frequently been found in various samples of Derbyshire lead, in Yorkshire lead, and lead from Snailbeach. Operating upon 2000 grains, he has found the following quantities of nickel in the pig-lead as delivered by the smelter:—

	Per cent.		ozs.	dwts.	grs.	
Derbyshire lead, 1st sample	0·0023	=	0	15	0	per ton.
Do. 2nd ,, ...	0·0031	=	1	0	0	,,
Do. 3rd ,, ...	0·0023	=	0	15	0	,,
Snailbeach lead	0·0007	=	0	4	13	,,
Softened slag-lead	0·0057	=	1	17	5	,,

On submitting lead containing these quantities of nickel to Pattinson's process, he found a concentration of the nickel in the liquid portion. In a 5-ton charge, crystals of lead were taken out in the proportion of $\frac{9}{10}$, leaving $\frac{1}{10}$ fluid lead.

Samples of the liquid lead or "bottoms," upon analysis, yielded nickel as follows:—

	Per cent.		ozs.	dwts.	grs.	
After 3 crystallizings	0·0047	=	1	10	16	per ton.
,, 1 ,, ...	0·0043	=	1	8	2	,,
,, 1 ,, ...	0·0062	=	2	0	12	,,
,, 2 ,, ...	0·0072	=	2	7	0	,,

In all cases a weighable quantity could be obtained from 2000 grains of lead.

In operating upon 5 tons of lead, containing 0·0068% of nickel (= 2 ozs. 4 dwts. 10 grs. per ton), 4½ tons were removed as crystals, which, after having been re-melted, contained only 0·0047% of nickel (=1 oz. 10 dwts. 1 gr. per ton). These figures show that nickel remains to a great extent with the liquid portion, much as copper does; and he states he has reason to suppose that when it reaches a certain amount, as is the case with copper, silver, and probably other metals, the separation is no longer effected, or only in a very small degree.

A sample of lead from 5 tons, when analysed, gave no indications of the presence of nickel; on crystallizing out $\frac{9}{10}$, the remainder gave distinct traces of the metal. In refined lead, he has only once succeeded in obtaining a weighable quantity, and only rarely found traces of nickel. That it is not removed by oxidation is proved by the larger quantity found in the fluid portion of the lead when crystallized, as well as by the fact that in the softened slag-lead which is submitted to the powerful oxidizing action of nitrate of soda, a considerable quantity of nickel is still found.

Antimony, tin, arsenic.—To Baker we owe the following observations: When 0·01% of antimony is added to soft lead, and the latter is subjected to crystallization, the pewter-white surface, which that proportion of antimony imparts to lead, does not disappear until after two crystallizations. At the third crystallization sample ingots *both from the crystals and the residual liquid lead*, presented the purple-tinted surface belonging to lead containing only a trace of antimony. Similar results were obtained from the addition of tin and arsenic added in just sufficient proportion to impart a white lustre to the lead. Mr. Baker informs me that he has reason to suppose that one metal influences the concentration of another; and that the *rich* lead, at the works with which he was connected, yielded a considerable residue by the action of nitric acid. He suspects that silver will aid the concentration of antimony, and antimony that of copper; but this latter suspicion is, I know, opposed to the experience of other observers.

Mr. Baker has supplied me with the following results obtained by himself in practice on the large scale, which are instructive and practically valuable to those treating lead of similar quality:—

CONCENTRATION OF COPPER IN PATTINSON'S PROCESS.

I. From 46 charges, representing nearly 270 tons of lead crystallized 8 times.

	Lead contained per cent.		
	Copper.	Iron.	Sulphur.
Before crystallizing	0·0125	0·0102	0·0208
After do.	0·0045	0·0113	0·0205

II. From three months' working.

	Lead contained of copper per cent.	
Before crystallizing	0·0113	0·0107
After do. 4 times	0·0081	0·0084
After do. 8 times	0·0037	0·0041

III. Results showing concentration of copper in residual liquid lead.

	Lead contained of copper per cent.		
	1st crystallizing.	2nd crystallizing.	3rd crystallizing.
Crystals	0·0027	0·0019	trace
Liquid lead	0·0137	0·0095	0·0159

IV. Results showing concentration of copper in residual liquid lead. In these operations only a very few cwts. of liquid lead were left; so that they do not show the concentration of copper so well as the foregoing.

	Lead contained of copper per cent.
Before crystallizing	0·0173
After do.	0·0115
Liquid lead	0·0391

V. Another charge of lead of which a single pig only was sampled, gave the following results:—

		Contained of copper per cent.
Before crystallizing		0·0774
After 4 crystallizings	Crystals	0·0574
	Liquid lead	0·0526
After 6 crystallizings	Crystals	0·0642
	Liquid alloy	0·0570

CONCENTRATION OF COPPER IN PATTINSON'S PROCESS, WHETHER INFLUENCED BY THE PRESENCE OF SMALL QUANTITIES OF SULPHIDE OF LEAD AND ANTIMONY.

Lead containing 0·0411% of copper, mixed with slag-lead (which contains both sulphide of lead and antimony, and, it may be added, other substances) in the proportion of 5 tons to 2 tons, was crystallized 7 times, after which it (*i.e.* the final crystals, not the residual liquid lead) yielded 0·0259% of copper.

A charge of the same soft lead, without the addition of slag-lead, was crystallized 7 times, after which it yielded 0·0239% of copper.

EXPERIMENT ON THE EFFECT OF THE ADDITION OF A SMALL QUANTITY OF ANTIMONY UPON PATTINSON'S PROCESS.

To a charge of 5 tons of lead 0·01% of antimony was added, which rendered the surface of the ingot white and crystalline, with brilliant facetted crystals. Before adding the antimony an ingot presented a yellow colour with fern-leaf forms of crystals. At the second crystallization a purple tint replaced the white, which in its turn, after succeeding crystallizations, gave place to a yellow colour inclining to a bronze-red tint.

		Contained per cent.		
		Copper.	Nickel.	Insoluble residue.
After adding antimony		0·0644	0·0062	0·1660
After 1st crystallizing	Crystals	0·0523	0·0047	0·1577
	Liquid lead	0·0664	0·0068	0·2085
After 2nd crystallizing	Liquid lead	0·0551	0·0072	0·4755
After 6 crystallizings	Liquid lead	0·0415	?	0·2865

This quantity of antimony appears to have no effect upon the separation of copper or nickel which are concentrated in about the same degree as would have been the case had no antimony been added. The quantity of insoluble residue roughly and only approximately indicates the proportion of antimony, and was obtained by evaporating to dryness the solution of lead in nitric acid and weighing at 100° C. It would seem that antimony when in this proportion concentrates in the liquid lead or "bottoms;" but this cannot be stated to be always the case, as the amount of copper and nickel present might have some influence in keeping antimony in the residual lead or liquid alloy.

EXPERIMENT ON THE EFFECT OF THE ADDITION OF A SMALL QUANTITY OF TIN UPON PATTINSON'S PROCESS.

Two pots containing 5 tons of lead each were submitted to 6 crystallizing operations.

A. With the addition of 0·00536% of tin.

B. Without tin.

		A.	B.
		Contained of copper per cent.	
Before crystallizing		0·0141	0·0173
After 1st crystallizing	Crystals	0·0111	0·0115
	Liquid lead	0·0470	0·0391
After 6 crystallizings	Liquid lead	0·0047	0·0047

The above small quantity of tin was quite sufficient to communicate a white appearance to the lead; but after the second crystallization the lead did not appear different from that of the other charge. These results show that the tin had no effect upon the separation of copper.

PARKES' PROCESS.

It has been stated[4] that when zinc and lead are melted together and the molten mixture is allowed slowly to cool, nearly complete separation of the two metals occurs, the zinc on account of its higher melting-point and lower specific gravity solidifying first and forming the upper layer, so that it may be removed as a crust from the liquid lead underneath. Mr. Alexander Parkes, of Birmingham, found that in the case of argentiferous lead the silver becomes concentrated in the crust of zinc produced under the circumstances just described; and this is the principle of his process for the desilverization of lead for which a patent was granted to him in 1850.[5] In the specification it is stated, that silver may be separated from lead by adding about 1 cwt. of zinc to every ton of melted lead; that as the mass cools the zinc crystallizes and abstracts the silver; that the zinc may be re-melted and again used until the proportion of silver abstracted amounts to 400 or 500 ozs. to 1 cwt. of zinc; and that the silver may be separated from the zinc by dissolving out the latter by hydrochloric or dilute sulphuric acid.[6] In 1851 Mr. Parkes obtained a second patent for "Improvements in separating silver from other metals," in the specification of which zinc is directed to be used in the following proportions:—

With a ton of lead containing	14	ozs. of silver	.....	22·4	lbs. of zinc.
,, ,,	21	,,	.....	33·6	,,
,, ,,	28	,,	.....	44·8	,,

As the alloy of zinc and silver rises to the surface during cooling, it is to be removed with a perforated ladle; the lead is freed from the zinc, which it retains, by being heated to dull redness with full access of atmospheric air, whereby the zinc is oxidized and may be skimmed

[4] See vol. i. of this work, p. 591.

[5] A.D. 1850. June 11. No. 13,118.

[6] Abridgments of the Specifications relating to Metals and Alloys, excepting Iron and Steel, 1861, p. 177.

off in the state of oxide along with any oxide of lead formed at the same time; and the zinc is to be separated from the silver by means of acids or by distillation.[7] A third patent was granted to Mr. Parkes in 1852 entitled "Improvements in separating silver from other metals." The special claim in the specification is heating "the alloy of zinc, silver, and lead" in perforated iron vessels, so that the lead may be drained off as much as possible from the solidified argentiferous zinc.[8]

In 1859 I first saw Parkes' process in operation at the works of Messrs. Sims, Willyams, Nevill & Co., Llanelly, and I am indebted to Mr. William Nevill, for the drawings from which the annexed woodcuts have been prepared, as well as for information concerning the cost of the process and other particulars. Shortly after my visit this process was discontinued. The entire process consisted of the following operations:—

I. Melting the argentiferous lead with zinc, skimming, and cooling.
II. Removal of the argentiferous zinc.
III. Liquation of the argentiferous zinc in order to separate as completely as possible mechanically entangled lead.
IV. Distillation of the zinc from the silver in a Belgian zinc-furnace.
V. Treating the lead, contaminated with zinc, in a softening-furnace, skimming, and poling.

Description of the apparatus.—Two vessels are used in No. I., a Pattinson pot of cast-iron capable of holding 7 tons of molten metal, for melting the lead, and a much smaller adjoining pot of the same kind for melting the charge of zinc. Each of these pots is, as usual, set over its own fire-place.

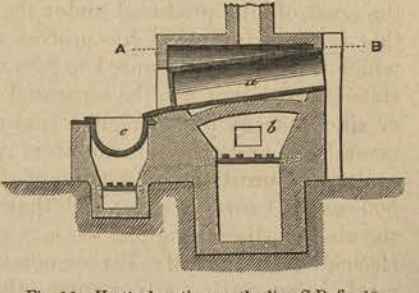

Fig. 16. Vertical section on the line C D, fig. 18.

The apparatus for liquation, No. III., is represented in figs. 16, 17, 18. It consists of a cast-iron retort, *a*, oval in bore, set a little inclined over a place, *b*, surmounted by an arched chamber of brickwork, and of a cast-iron pot, *c*, likewise set over a fire-place. At the bottom of the closed end of the retort is a hole through which the liquated lead may flow into the pot, *c*. The upper end of the retort is open, and there the charge of metal is introduced.

The distillation-furnace for No. IV. was small, and consisted of two series of Belgian retorts, one on the right and the other on the left, with a central fire-place common to both.

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[7] Op. cit. p. 189. A.D. 1851. June 24. No. 13,675.
[8] Op. cit. p. 197. A.D. 1852. March 8. No. 13,997.

The softening furnace for No. V. is represented in figs. 19, 20, 21, 22. The bed *a*, *a*, is of cast-iron in one piece, having a tap-hole, *d*, on one side; its border at the narrow end is $2\frac{1}{4}''$ thick, and is purposely made somewhat thicker than elsewhere, as the skimmings are drawn out over this end; the total weight of the cast-iron bed is 4 tons. It rests upon a thin course of brickwork, built on wrought-iron bars placed longitudinally and supported by transverse cast-iron girders, *c*, *c*, *c*, *c*, see figs. 19, 21. There is a circular cast-iron pot, *e*, *e*, to receive the lead when tapped out; it is set over its own fire-place, communicating with an underground flue by the flue, *f*, *f*, fig. 22. The other details of construction may, it is conceived, be so clearly apprehended from inspection of the woodcuts as to render a description of them unnecessary.

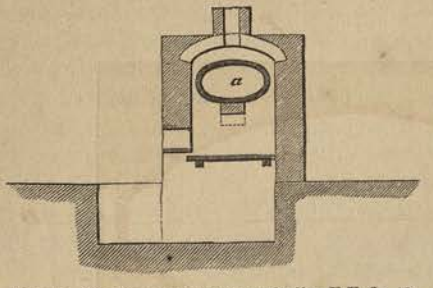

Fig. 17. Vertical cross-section on the line E F, fig. 18.

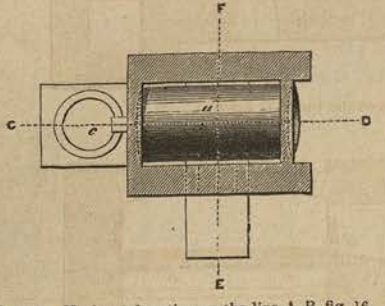

Fig. 18. Horizontal section on the line A B fig. 16.

Description of the process.—A charge of 7 tons of the lead to be desilverized is melted in the Pattinson pot, "boiled" by the immersion of wood and skimmed. The weight of the skimmings is 5 cwts.

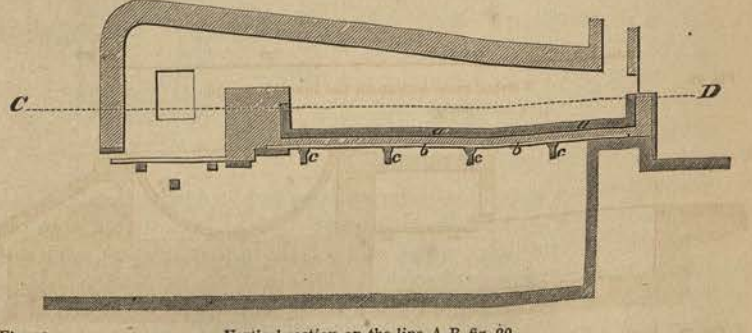

Fig. 19. Vertical section on the line A B, fig. 20.

The temperature of the lead is raised to the melting-point of zinc, and then the charge of zinc previously molten in the adjoining small pot is laded into the lead. The practical smelter of these works informed me that $1\frac{3}{4}$ lb. of zinc was required for every ounce of silver; but in

the tabulated statement of the cost of the process, by Mr. W. Nevill, which will follow, the proportion of zinc is very much less. The molten mass is stirred well with a perforated rabble, so as to cause

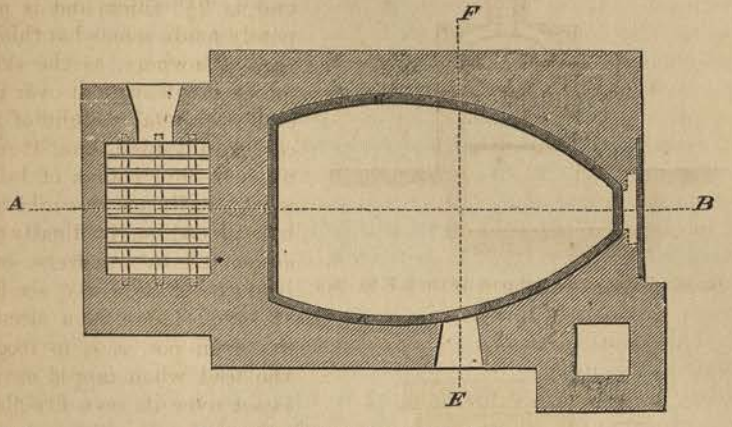

Fig. 20. Horizontal section on the line C D, fig. 19.

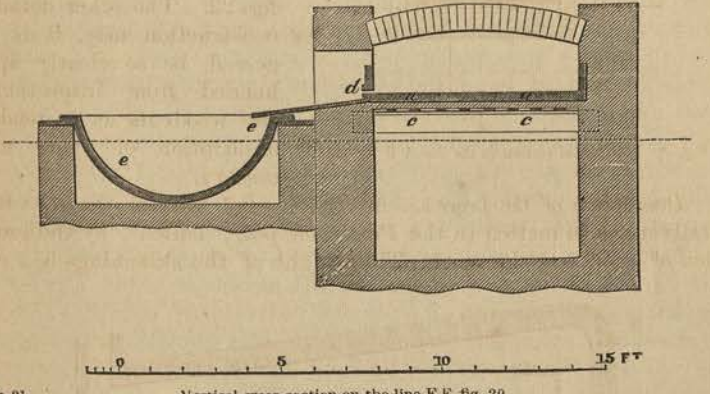

Fig. 21. Vertical cross-section on the line E F, fig. 20.

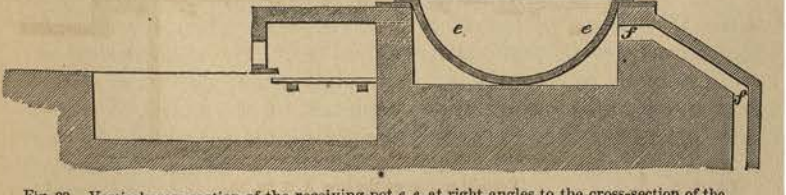

Fig. 22. Vertical cross-section of the receiving-pot *e*, *e*, at right angles to the cross-section of the same pot in fig. 21.

thorough intermixture of the two metals; the fire is damped, and the mass left to cool gradually. During cooling the zinc must be kept from adhering to the sides of the pot by means of a piece of wood, so

as to prevent the formation of a solid ring of zinc round the pot. When the surface has hardened it must be skimmed with a perforated ladle. After taking off the solidified zinc the subjacent liquid lead is skimmed. After this treatment the surface of the lead has a rich indigo-blue colour, with which I was much struck. After removing the zinc the lead should be assayed for silver, and if too much of the latter metal be found, the lead should be left at rest for an hour and then skimmed again. The lead thus desilverized contains about 10 dwts. of silver per ton, and requires to be softened in order to fit it for the market. According to recent experience at other lead works the proportion of silver will rarely be found so low as 10 dwts. A specimen of the zinc crust, which I brought from the works, contains 0·69% silver, *i.e.* 225 ozs. 8 dwts. per ton. The fracture is finely granular, somewhat uneven, approximating to conchoidal, and blueish-grey; particles of lead are adherent to its upper and lower surfaces.

The solidified zinc is put into the liquation-retort and there heated somewhat above the melting-point of lead, but sensibly below that of zinc. A specimen of the liquated lead contained 55 ozs. of silver per ton, whereas, according to Mr. Nevill, it ought not to have contained more than 10 ozs. per ton. The residual zinc, if the operation has been properly conducted, will retain from 40% to 50% of lead, but no more. The liquated lead is put aside until sufficient has accumulated to fill the large Pattinson pot, when it is melted, skimmed, and otherwise treated as in the operation previously described, but no fresh zinc is added as the lead retains sufficient for the purpose.

The zinc thus drained of lead as far as practicable is distilled in the Belgian retorts, in admixture with twice its bulk of lime and its own bulk of coal, 5 cwts. of zinc constituting a charge for the furnace. I was assured that no sensible quantity of silver was volatilized along with the zinc; but supposing any silver to be carried over, it would not be lost, as the zinc is used in the next operation. The residue in the retorts consists of lead and pulverulent matter. The lead is re-melted, skimmed, and cupelled. The skimmings and powder are added to the charge in a lead ore-smelting furnace. The process of distillation lasts about 24 hours. There is great loss of zinc throughout the whole process at almost every stage.

The charge of desilverized lead, in the softening process, is 10 tons. It is kept melted at a good red-heat. The duration of this process varies with the quality of the lead. The time needed, on the average, for its completion is 9 hours, but sometimes it is protracted to 12 hours, and at other times completed in 6. A sample should be withdrawn from time to time and tested as to its softness. The lead is generally skimmed twice, the first time about 3 hours after charging, and the second time about half an hour before tapping. Some varieties of lead will throw up much more skimmings than others. During the first 2 hours it is heated more strongly. The lead is tapped off into the cast-iron receiver, and therein subjected to "boiling," *i.e.* wood is kept submerged in it, just as in the analogous operation in the refining of tin. The wood is held down by the

simple contrivance of a lever, fixed at one end, and weighted or otherwise depressed at the other end, a rod of iron descending vertically from about the middle of the lever, and having attached at its lower end a convenient apparatus for holding the wood. The "boiling" process is continued for about an hour. We found 4 ozs. troy of silver per ton in the lead desilverized as above, but no zinc. The effect of the ebullition due to the escape of the gaseous matter from the wood, thus heated considerably beyond the temperature at which it begins to decompose, is probably not wholly mechanical. Much steam is evolved from the wood, and steam at a red-heat would oxidize zinc with the evolution of hydrogen; and a method of applying steam with the object of dezincifying the lead desilverized by Parkes' process has been proposed and carried out by Cordurié, which will be hereafter described.

The softened lead, I was informed, was *not completely* skimmed before tapping. Some shovelfuls of fine culm are thrown on before skimming in order to facilitate the operation, as the matter to be thus drawn off is too thin to be skimmed without the addition of culm. The matter left after tapping tends to prevent the cracking of the furnace-bottom.

Cost of the process.—The following details were communicated to me by Mr. William Nevill, with permission to publish them (April, 1859):—

	£	s.	d.
Mixing 80 tons of lead containing 15 ozs. of silver per ton with zinc, softening, lading, &c.	5	2	0
Coal, iron, wear-and-tear, &c.	3	10	0
Spelter required for the above quantity of lead, 1063 lbs., at 2*d.* per lb.	8	17	2
Concentrating silver alloy and softening lead from do.	0	18	6
Calcining and reducing 3 tons of dross from 80 tons of lead	1	15	0
Distilling 30 cwts. of silver alloy from 80 tons of lead	3	15	0
Melting rich residue from distilling retorts, and preparing for refining	0	6	0
Refining rich silver lead	0	15	0
	24	16	8
Add value of lead lost, about 1%	16	4	0
	41	0	8
Cost per ton	0	10	1

Recent experience at other works has shewn the cost here given to be too low.

Karsten's experiments on Parkes' process.—Karsten announced that in 1842 he arrived at the conclusion from experimental data that lead gives up its content of silver to zinc in proportion as a melted mixture of lead and zinc is exposed during solidification to the condition most favourable to the complete separation of the two metals, *i.e.* slow cooling; but it did not occur to him to apply that conclusion to practical metallurgy.[9] In 1851 Karsten was informed that the

[9] Archiv, 1853, 25. p. 196.

desilverization of lead by zinc was being carried out in Wales when he suggested that experiments on a large scale should be forthwith made at the Friedrichshütte (Frederick Smelting Works belonging to the Government) at Tarnowitz, in order to test the economical value of the process. The suggestion was complied with, and the following is a summary of the chief results obtained. I have not considered it necessary to reduce the Prussian weights into English. The centner or hundredweight is 100 lbs. Prussian, or 103·111 pounds avoirdupois.[1] The loth is about 225 troy grains, say roundly half an ounce troy. The apparatus used was a Pattinson pot of cast-iron; and it was provided with an upright rake-like stirrer of wrought-iron which might easily be turned right and left so as to mix the lead and zinc as intimately as possible, and which, after the end of the stirring, might easily be withdrawn from the pot, in order that it might not interfere with the solidifying argentiferous zinc.

I. 20 ctrs. of 4¼-loth lead (*i.e.* containing 4¼ loths of silver per ctr.) were melted, then alloyed with 1 ctr. (5%) of zinc, covered with charcoal-powder, and kept during 2 hours at a moderate melting heat, during which period the stirrer was in constant motion. After the stirring the temperature of the metallic bath remained the same, except towards the end of 6 hours when it was lowered, water being sprinkled on the surface in order to solidify the upper layer of metal. The solidified metal was removed, and the liquid lead laded out; the latter was completely desilverized, as it retained only $\frac{1}{64}$ loth of silver per ctr.

II. 20 ctrs. of 3-loth lead were alloyed with 1 ctr. of zinc at a stronger heat, and subjected to the same kind of manipulation as in No. I. The stirring period lasted only an hour, after which the metallic bath was left at rest during 4 hours. The lead was quite free from silver.

III. 20 ctrs. of 3-loth lead were alloyed with ½ ctr. (2½%) of zinc, and treated as in No. II. Complete desilverization is stated to have occurred.

IV. 20 ctrs. of 2½-loth lead were alloyed with $\frac{3}{16}$ ctr. ($\frac{3}{4}$%) of zinc, and treated as in No. II. The lead was not completely desilverized, but retained ½ loth of silver per ctr.

Many similar experiments were made in order to find the minimum of time and of zinc required for desilverization, so as at least not to leave more than $\frac{1}{64}$ loth per ctr. in the lead. The result shewed that by proceeding as above described, stirring during an hour and the addition of 1½% of zinc must be regarded as the minima, and that the time required for the completion of the whole process in a pot containing 25 ctrs. is not less than 4 hours.

Karsten then suggested a different mode of conducting the process, namely, that the whole metallic mass should be left to solidify in the pot, and then so gently re-heated as only to liquefy the de-

[1] In 1858 the Prussian pound was altered, and the centner made equal to 110·232 lbs. avoirdupois.

silverized lead, from which the superjacent argentiferous zinc crust might be taken off. But in this method the fusion could not be so managed as to be restricted wholly to the desilverized lead. Moreover the greater consumption both of time and fuel in this method would be adverse to its adoption in practice.

The next notion was to employ a Pattinson pot, with a vertical slot at the upper part, which might be stopped, say with bone-earth, such as refining tests are made of. An opening might be made in any part of this slot, so that the argentiferous molten metal might be drawn off at the top or lower and lower until perfectly desilverized lead should begin to flow, and then the tap-hole should be instantly closed and the lead laded out. But an unexpected difficulty occurred. As soon as the hole in the slot approached the level of the desilverized lead, this began to flow out, being pressed by the superincumbent, less fusible, and tougher argentiferous alloy, which then no longer escaped.

The last idea was cautiously to draw off the desilverized lead through a cast-iron pipe $1\frac{1}{2}''$ in diameter, inserted on a level with the bottom of the pot. This pipe passed outwards through the surrounding brickwork, and at the end where it entered the pot there was a slide-valve contrivance attached to an iron rod extending upwards through the metal to a convenient height above its surface, so that the hole at the bottom might be conveniently opened or closed according to circumstances. With this arrangement of pot, the following results were obtained.

V. 25 ctrs. of $1\frac{3}{4}$-loth lead were alloyed with 4 ctrs. of zinc, and stirred during an hour at a strong red-heat. The special object was to tap out the desilverized lead, and leave the argentiferous alloy in the pot, which might forthwith be used for a second desilverization, and so on up to a certain limit; and it is rather an advantage than otherwise of this method, that sufficient lead may be left in the pot to make sure that no silver escapes through the tap-hole. After the stirring and the metallic bath had been kept at a red-heat during 4 hours, metal was drawn off until only 6 ctrs. remained in the pot, when the tap-hole was closed. A second charge of 25 ctrs. of $1\frac{3}{4}$-loth lead was added to the residual metal in the pot. The metal was again drawn off until only 6 ctrs. were left in the pot. The lead was perfectly desilverized. The third time 25 ctrs. of $1\frac{3}{4}$-loth were put into the pot and 2 ctrs. of zinc. The metal was tapped off until only 6 ctrs. remained in the pot. The lead was free from silver. The fourth time the same addition was made, and the same treatment followed as in the third. The lead was perfectly desilverized. For the fifth and sixth time the same course was repeated, but without the addition of fresh zinc, and in both cases the lead was completely desilverized. For a seventh time this course was repeated without the addition of fresh zinc; but the lead drawn off was no longer desilverized, and retained $\frac{3}{4}$-loth of silver per ctr.

It appears from the first six trials (the seventh being left out of

consideration as it was a failure) that 5⅓% of zinc was required to desilverize 1¾-loth lead, whereas in the preceding experiments, with a single fusion, only 1½% of zinc was needed for that purpose.

Karsten assigned several reasons for the unfavourable results last recorded. Although the surface of the molten metal may be kept covered with charcoal, yet, owing to the constant and long-continued stirring, a large quantity of dross, consisting of the oxides of zinc and lead, intermixed with particles of charcoal and shots of metallic zinc, is always formed. This metallic zinc is so much virtually withdrawn from the pot; and not only can it not contribute to the desilverization of the lead, but it carries off any silver which it may have previously abstracted. The evil would be removed by excluding atmospheric air, which would be very difficult, if indeed it be practicable. In any case it is essential to effect the most intimate mixture of the lead and zinc, and this cannot be done without much stirring. Experiments in the laboratory did not, says Karsten, suggest the fear that the formation of dross or scum would be the rock on which the process on the large scale would be wrecked. One thing, however, is certain, there can be no loss of silver by volatilization, as no evaporation either of lead or zinc takes place at the temperature at which the operation is performed, and *à fortiori* there can be none of silver.

The separation of the zinc from the lead is not perfect [and this is really the point on which the process was wrecked, not the drossing]. Karsten made the following experiments on the mixture of lead and zinc in a pot after the completion of the usual treatment, namely, stirring, skimming, and leaving at rest until the lead was ready to be drawn off below. The uppermost and most argentiferous layer contained, besides zinc and silver, 2% of lead. At 1¼″ below the surface, the metal contained 8·6% of zinc, and ½″ deeper 2·5%; and below this layer the desilverized lead was soon reached, which still contained ¾%[2] of zinc even to the bottom of the pot. The proportion of zinc thus remaining in the lead was not influenced either by the quantity of zinc added, or by the higher or lower temperature at which the process was conducted; and that proportion of zinc is quite sufficient to render lead unsuitable for various purposes of manufacture, for example, that of pipes; though there are others, such as the manufacture of white-lead or shot, in which such lead might be used with advantage. [This statement is wrong, as zinc would be fatal in shot making and bad for white-lead making.] Lead cannot be perfectly freed from zinc, even at a high temperature; and the lead remaining in the retorts of the Silesian zinc-furnace, has been found impregnated with a notable quantity of zinc.

With a view to remove the difficulty arising from the formation of so much dross, consequent on stirring with access of atmospheric air, Lange, the smelter at the Tarnowitz Lead Works, contrived

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[2] If the separation had been properly effected, ¼% would be nearer the truth.

another mode of intimately mixing the zinc and lead together. [There is not the slightest difficulty in mixing lead and zinc in open pots without any oxidation, practically speaking.] Each metal is melted in a separate vessel, and skimmed clean; and that containing the zinc is cylindrical, and higher than wide. The lead is then poured into the zinc through the same kind of apparatus as is used in manufacturing shot, or through an iron plate perforated with holes $\frac{1}{30}''$ in diameter, so that it descends through the zinc in small drops. After the addition of the lead, the metallic mixture is left at rest for about 3 hours, and then the lead is drawn off through a pipe at the bottom in the manner previously described. To the residual zinc a second charge of lead is added, and so the process is repeated several times, but not beyond the period when the zinc contains 25% of silver. It need hardly be added that the quantity of zinc added in the first instance must be properly adjusted to the total quantity of lead to be desilverized. None of the lead after desilverization contained less than $\frac{1}{4}$% of zinc. Karsten speaks favourably of Lange's method.

There was mixed with the argentiferous zinc sufficient lead for the cupellation of the silver, after the distillation of the zinc in a Silesian zinc retort; but the loss of silver was considerable, notwithstanding the quantity of lead which was left along with it in the retort. It was ascertained that no silver was carried over with the vapour of zinc, at least not when it was alloyed with lead in the retort. As sufficient lead was always necessarily left in the retort to alloy with the silver, no opportunity was afforded of learning, whether, in the absence of lead, silver would have been volatilized along with the zinc. The loss of silver was found to be due to the escape of the argentiferous lead through the stopping in the hole in front of the retort, through which the exhausted residue is raked out; yet this stopping effectually retained the ordinary quantity of lead left in the distillation of zinc ore containing lead. Retorts were then made with a dam 4″ high at the bottom in front, and in the dam was a tap-hole $\frac{3}{4}''$ in diameter. From four distillations in two retorts of 4 ctrs. of the argentiferous zinc, which after the most careful assaying was found to contain $94\frac{1}{2}$ loths of silver, 242 lbs. of lead containing $88\frac{9}{32}$ loths of silver were collected. The loss of silver amounted to $6\frac{1}{1\,1}$ loths; but this was owing to the dispersion of the silver, chiefly in small globules in both retorts, and also in the residue, from which however in subsequent distillations by washing, or by other suitable treatment, the lost metal will be recovered. The desilverization of the zinc by distillation is, as Karsten observes, not the least difficulty connected with this process.

The cost of the process, per 100 ctrs., was estimated by Lange as follows:—[3]

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[3] This table shows but a small part of the actual cost of the process.

	Thalers.	sgr.	pf.		£.	s.	d.
2½ loths of silver lost, at 26 sgr. 3 pf.	2	5	7	.....	0	6	6½
½ ctr. of lead lost, at 6 thalers	3	0	0	.....	0	9	0
½ ctr. of zinc lost, at 4 thalers 20 sgr.	2	10	0	.....	0	7	0
Labour	1	22	6	.....	0	5	3
Fuel	4	0	0	.....	0	12	0
	13	8	1		1	19	9½

The cost therefore is about 8 shillings per ton of lead desilverized. The zinc is not lost but is used over again, so that its cost is properly excluded from the foregoing account. The cost of softening the desilverized lead is not included, as in Mr. Nevill's account previously given. Karsten concludes by stating that the small loss of metal in this process is its most important advantage [whereas it is the *large* loss that is the greatest drawback of the process]; that lead too poor in silver to be treated by cupellation may be profitably desilverized by zinc; and that the small quantity of zinc left in the lead may undoubtedly be removed by refining.

Desilverization of argentiferous lead by zinc has again been taken up in Germany in 1866, and, it is asserted, with more favourable results than previously, when it was abandoned for three reasons: first, on account of the difficulty of freeing the lead treated from the zinc which it retained, so as to render it marketable [whereas the fact is, there is no difficulty, and zinc is the easiest metal to separate from lead]; secondly, of extracting the silver from the crust of zinc without loss; and thirdly, of separating the lead from the zinc, so as to fit it for practical uses.[4] Since 1866 the process has been in operation in the Eifel, at the works of Pirath and Jung, at Commern, and at those of Herbst and Company at Schliessemaar, near Call, the proprietors of which, we are informed, were compelled to take this course from the difficulty of procuring and retaining workmen possessing the necessary skill to conduct the Pattinson process!

At the works above mentioned the process is carried out as follows: The lead is melted in a Pattinson pot and heated sufficiently to fuse a piece of zinc placed on the surface of the molten lead. The zinc is added in three portions, first ⅔ of the total quantity required, then ¼, and lastly $\frac{1}{12}$. After the addition of the first portion, the two metals are intimately mixed by stirring with a perforated ladle during 20 or 30 minutes, the temperature being well kept up during that period. The fire is now damped with wet fuel, and the pot is left to cool. The solidified crust of zinc, which collects on the surface, is taken off, any portions which may adhere to the sides of the pot are detached, and the operation of skimming is continued until the lead begins to crystallize and set strongly on the sides of the pot. The temperature of the pot is again raised to the melting-

[4] A paper on the subject has been communicated by Illig, of Andreasberg, to the 'Zeitschrift für das Berg-, Hütten- u. Salinenwesen in dem Preussischen Staate,' 1868, B. 16. p. 49; and from that paper the following information has been derived. I shall translate literally much of what Illig has written.

point of zinc, and the second portion of zinc is put in, the same manipulation being practised as in the first instance. The third portion of the zinc is added, and the same treatment followed; but in this case more care is needed in skimming than in the two preceding operations on account of the richness in silver of the zinc removed. The special precautions to be observed are, heating the lead under treatment very hot and intimately mixing the zinc with it, cooling the lead very slowly,—very careful skimming and taking care to prevent pieces of the crust of zinc from dropping into the pot and becoming re-melted in the subjacent lead.

The charge of zinc is regulated according to the content of silver in the lead. For complete desilverization the following proportions have been found necessary:—

Lead containing	250	grammes of silver	per 1000 kilogrammes	requires	$1\frac{1}{4}\%$ of zinc.
,,	500	,,	,,	,,	$1\frac{1}{3}$,,
,,	1000	,,	,,	,,	$1\frac{1}{2}$,,
,,	1500	,,	,,	,,	$1\frac{2}{3}$,,
,,	3000	,,	,,	,,	2 ,,
,,	4000	,,	,,	,,	2 ,,

From the foregoing table, it will be perceived that the quantity of zinc required is not proportionate to the quantity of silver in the lead, for which no reason can yet be assigned; and the correctness of the numbers given has been confirmed by trials made at the Clausthal Silver Works. Thus, at these works, it was found that, whereas $1\frac{2}{3}\%$ of zinc sufficed to desilverize lead containing 1250 grammes of silver per 1000 kilogrammes, $1\frac{1}{2}\%$ did not; in the former case the silver amounted to 5 grammes, and in the latter to 10 grammes per 1000 kilogrammes of lead.

The quantity of silver abstracted after the successive additions of zinc is very variable, and is not the same at different works, as the following results will show:—

	I.	II.	I.	II.
	Silver in grammes per 1000 kilogrammes of lead.		Relative proportion of silver abstracted after each addition of zinc, estimating the total = 100.	
Original lead	283	1250	100	100
Lead after 1st addition of zinc	210	250	74	20
Do. 2nd do.	50	42	17	3·36
Desilverized or poor lead ...	6·2	5	2·2	0·4

I. Results obtained by Illig at the Schliessemaar Works.

II. Results obtained at the Clausthal Silver Works.

In No. II., where lead much richer in silver than in No. I. was operated upon, desilverization was more quickly effected than in No. I., contrary to what was anticipated; and it has also been found that less zinc suffices for the desilverization of the poorer argentiferous lead of Clausthal, and that only two additions of zinc are

required. As the zinc crust taken off after the second and third additions is not saturated with silver, it may be used again to desilverize instead of fresh zinc; and at Schliessemaar this is sometimes done without rendering desilverization less complete.

Dezincification of lead by chloride of lead.—The novel part of the process of desilverizing argentiferous lead by zinc, which has been introduced in Germany, is the removal of that portion of the zinc which is retained in the poor lead produced, whereby the latter may be rendered fit for practical uses.[5] This consists in subjecting the poor or zinciferous lead while melted to the action of substances containing chlorine, especially chloride of lead, for which a patent has been granted to Herbst, and an engineer of the name of Wassermann.[6] After the completion of the process of desilverization, in the manner above described, the poor lead is kept melted during usually about 24 hours, at a moderate temperature in a Pattinson pot under a layer of 3½% of chloride of lead, (*i.e.* 3½% by weight of the lead under treatment), when by frequent stirring the zinc existing in the lead is converted into chloride with the separation of an equivalent proportion of metallic lead from that salt. The chloride of zinc thus formed swims upon the surface of the metallic bath in a slag-like state. At Herbst and Co.'s works, where this operation is conducted, the chloride of lead is prepared by the action of hydrochloric acid upon lead-fume, and is, consequently, not very pure, containing only 62% of lead, instead of 74%, the theoretical proportion in the pure chloride. It is applied while still moist. The complete removal of the zinc is indicated by the lead presenting the appearances characteristic of purity, which are well known to every experienced lead-smelter, and amongst these may be particularly mentioned the iridescent skin. The lead is then skimmed clean, after throwing on a little lime in order to thicken the chloride of zinc slag, and if it be free from antimony [in which case the treatment with chloride would be useless, as the zinc would be separated by calcination during a few hours], it is, after this treatment, ready for sale; but if not, it must be kept at a dull red-heat in a softening furnace during 24 hours. (See the article on softening hard lead in the sequel, p. 458). In the case of antimonial lead it would probably be better to resort to this process in the first instance, as along with antimony zinc would be separated in an oxidized state. The changes in composition which the lead at Herbst and Co.'s works undergoes in this double treatment are shown in the following tabulated results of Illig:—

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[5] I wish it to be distinctly understood that, while I publish the following statements, I do not assent to many of them. For the comments between the brackets, [ ], I am responsible.

[6] According to Gruner, at Braubach, on the Rhine, the argentiferous crusts of zinc are treated with chloride of lead, as well as the desilverized lead. Chloride of zinc is formed, and the silver is concentrated in the lead, which in part existed in the crusts, and is in part derived from the chloride of lead reduced by the zinc. Ann. d. Mines, 6. ser. 13, p. 393. 1868.

	Foreign metals contained in the lead per cent.		
	I.	II.	III.
	Desilverized or poor lead.	Dezincified poor lead before softening.	Market lead after softening.
Antimony	0·046	0·010*	0·003
Copper	0·008	0·011	0·007
Iron	0·004	0·005	0·005
Zinc	0·777	0·005	0·003
Silver	0·00062	0·00062	0·00062

* In the original paper the number given is 0·070, which, as the context shows, is clearly a typographical error.

From the foregoing results, it appears that during the dezincification of the lead, antimony is in a certain degree abstracted, having been reduced from 0·046% to 0·01%, and as Illig suggests by the formation and volatilization of chloride of antimony, or by its oxidation by the free oxide of lead existing in the chloride of lead employed. On the contrary, the proportion of copper is increased, in the instance given, from 0·008% to 0·011%; and this result is ascribed by Illig to the derivation of copper from the impure chloride of lead containing that metal [but like many other results, it may have arisen from error of analysis or of sampling].

Dezincification of lead by other chlorides.—At the lead works of Pirath and Co., at Commern, the zinciferous poor lead is kept melted under a layer of 1% of common salt in a reverberatory furnace during 8 or 10 hours [recent experience in England shews that without common salt the lead would have been ready for tapping in 4 or 5 hours], poling being at the same time practised, after which the lead is tapped off into a pot, skimmed, and laded into pig-moulds. According to laboratory experiments by Illig on this subject, oxide of lead is produced, which evolves chlorine from the chloride of sodium, with the formation of a compound of oxide of lead and soda. The chlorine thus set free combines directly with zinc and lead, producing chlorides of those metals; and then the chloride of lead performs the same function as previously described. Illig ascertained that by melting pure oxide of lead (PbO) in admixture with chloride of sodium, perfectly free from sulphate of soda, chloride of lead is formed.

Lead, resulting from the treatment by chloride of sodium, was found to have the following composition [but no proof is advanced to shew that the composition of the lead was in the least influenced by the chloride of sodium]:—

Composition of Lead per cent.	
Copper	0·0021
Antimony	0·0028
Iron	0·0179
Zinc	trace

At the end of 1867 and beginning of 1868 experiments were made at the Royal Silver Works at Clausthal, on the substitution of the potassic chlorides of the saline deposits at Stassfurth for chloride of

lead and common salt. With this object the desilverized lead was kept melted with frequent poling during 24 hours in a Pattinson pot under a layer of 2% of those salts, which contain chloride of magnesium. Now, as the latter salt evolves hydrochloric acid when strongly heated, it was anticipated that this acid would promote dezincification. The anticipation was, it is stated, confirmed by practice; the results were quite as satisfactory as with chloride of lead, and what is important, there was no production of noxious vapour like that of chloride of lead (?). A mixture of sulphate of lead and Stassfurth salt has been found more advantageous than either chloride of lead or alkaline chloride by itself, as the purification of the lead is much sooner effected by the former than by either of the two latter. The results obtained with the use of this mixture of sulphate of lead and Stassfurth salt are given as under:—

FOREIGN METALS CONTAINED IN THE LEAD PER CENT.

Original lead.	After heating 12 hours in a Pattinson pot.	After heating 24 hours in a Pattinson pot.	Softened in a German cupellation-furnace.
Copper ..... 0·1070	..... 0·0054	..... 0·0064	..... 0·0062
Antimony..... 0·6208	..... 0·0096	..... 0·0080	..... 0·0058
Iron ..... 0·0032	..... 0·0034	..... 0·0019	..... 0·0018
Zinc ..... 0·0013	..... 0·0034	..... 0·0024	..... 0·0024
Silver ..... 0·1200	..... 0·00063	..... 0·00063	..... 0·0013

Another mode of dezincification.—According to Illig, this consists in passing the desilverized lead, with the addition of sand and tap-cinder (*i.e.* basic silicate of protoxide of iron from the puddling-furnace), through a small blast-furnace. Most of the zinc is thus slagged off, and the rest volatilized. The lead is tapped into an iron pot and poled during an hour in order to remove the last portions of zinc. Lead thus produced has been found to contain the following foreign metals per cent.:—

	I.	II.
Iron.....	—	0·004
Zinc	—	0·003
Antimony	0·0015	0·002
Copper	trace	0·006
Silver.....	0·0004	0·0009

I. Analysis by Eisenhuth. II. Analysis by Illig.

It is, however, asserted that the chemist Flach, who was reported to adopt this method, kept his proceedings secret. But Flach obtained a patent in England for alleged improvements in extracting silver from lead, and in the specification this process is described.[1]

[1] A.D. 1866, Dec. 31st. No. 3449. Flach died in 1868. His patent furnishes another illustration of the absurdity of the existing patent laws, and shows the necessity of the exercise of discretion on the part of the crown in the granting of patents. It is certain that if it had been required to submit the specification to a competent tribunal and obtain its approval as a condition, this patent would not have been granted, at least in its present shape. Methods are claimed which had been long previously patented and applied in practice in this country. The use of the blast-furnace seems to be the essential point; and yet in the specification it is admitted that without the blast-furnace, the whole of the zinc may be re-

Treatment of argentiferous zinc. — The third and last operation, which remains to be considered, is the extraction of silver from the zinc. A considerable quantity of lead is always removed along with the zinc, from which it is partially separated by liquation. The apparatus used for this purpose consists of two cast-iron pots, one placed over or at a higher level than the other. In the bottom of the upper pot is a pipe, with an arrangement for opening and closing it. The zinc skimmings are melted down at a strong heat in the upper pot, when the lead liquates and collects at the bottom; while the greatest part of the argentiferous zinc residue swims as a powdery mass (staubförmige Masse) on the surface of the molten metal. The lead is tapped from the upper into the lower pot, the argentiferous zinc residue remaining in the former. As the liquated lead carries with it a little silver and zinc, it is slowly cooled and skimmed; and these skimmings are also liquated. The residual lead is now very poor, and is added to the original lead used in the first process of desilverization before the introduction of the third portion of zinc. The lead separated by liquation from the argentiferous zinc, and previously to the subsequent skimming, contained, according to the analysis of Michaelis, the following metals per cent:

	I. Composition of Liquated Lead.	II. Original Lead.
Antimony	0·128	0·035
Copper	0·018	0·161
Iron	0·005	0·005
Zinc	0·998	0·006
Silver	0·050	0·0283

For the sake of comparison, the analysis of the original lead is inserted under No. II. The concentration of antimony in No. I. should be noted, as well as the decrease in the proportion of copper, which shows that the latter has been removed in a notable degree by the zinc. The liquated argentiferous residue of zinc consists partly of powdery oxides of lead, zinc, &c., and partly of the alloys of those metals in lumps. The quantities of residues obtained at the Eifel Works in operating upon argentiferous lead of different degrees of richness were as under:—

Content of silver in grammes per 1000 kilogrammes of the lead operated upon.	Quantity of zinc residue per 100 of lead operated upon.
250	2
1000	4
3000	6
5000	7
8000	9

moved from the desilverized lead by calcining and poling, as practised at the Llanelly Works in 1859. It is stated in the specification that "up to this time it was unknown that zinc could be completely removed from lead by the use of green wood; steam can also be employed." It is asserted that in Flach's so-called system complete desilverization of the lead is effected, "an entirely pure lead is obtained, and there is in addition a gain of from 3 to 4 per cent. of silver as compared with the old mode of treatment by Pattinson's process" (!)

The argentiferous zinc residues are smelted in conjunction with lead and tap-cinder in a low blast-furnace, with coke as the fuel; and the lead is tapped off in which the silver is concentrated. This is refined in an English cupellation-furnace. Trials have been made with the view of further concentrating the silver, by subjecting the rich argentiferous lead from the blast-furnace to desilverization by zinc; but they were not successful, as in that case the loss of silver was increased more than in proportion to the richness of the products obtained.

A pamphlet in French, by Sièger, on the subject of Flach's so-called system, has appeared since the above was in type, which contains somewhat surprising announcements in its favour. It is declared that the silver extracted by it exceeds by at least 2% the total indicated by assay, that the loss of lead is "almost inappreciable" (*presque inappréciable*), and that it is "45 per cent. more economical than Pattinson's system and every other." This statement, with respect to economy, is contained in a certificate of Guillem and Co., of Marseilles, dated July 15, 1869, a firm engaged in the desilverization of argentiferous lead, especially that of Spain. They also certify that they had carried on Flach's process for nearly three years, that they concentrated the silver in the lead for cupellation to the extent of 9%, and that during a year and a half they had adopted Flach's process to the exclusion of every other. Another certificate, dated Jan. 21, 1869, is given by the manager of the Par Smelting Works, Cornwall, to the following effect: that since August 27, 1869, the quantity of argentiferous lead treated at those works was 1013 tons, and the quantity of silver produced was 59,300 ozs., the excess of silver beyond what was indicated by assay being 1024 ozs., exclusive of from 300 to 400 ozs., computed to remain in the hearth of the blast-furnace. I have given the dates as they occur in the pamphlet, though there is obviously a blunder. It is necessary to bear in mind that assaying, especially of argentiferous products, has not always been accurately conducted, and that seriously erroneous conclusions concerning metallurgical processes have sometimes resulted from such inaccuracy. Flach's so-called system consists of the following operations:—1. The addition of zinc to the argentiferous lead in three successive portions, with the usual precautions, the crust being removed in due time after each addition, and liquated in order to separate adherent lead; 2. Drawing off of the desilverized lead from the bottom of the pot; 3. Passing the desilverized lead through a blast-furnace, in conjunction with slags consisting of silicate of protoxide of iron, or of this oxide, lime and alumina, and containing about 33% of silica; and it is recommended that the pressure of the blast should not exceed 6·4 inches of water; 4. The lead from the furnace is poled with greenwood, in order to remove the zinc which it may still retain; or calcining in a softening furnace, and subsequent poling may be resorted to instead; 5. The argentiferous zinc crusts, after having been liquated, are passed through a small blast-furnace in conjunction with slag containing about 36% of silica, with

a pressure of blast equal to 7 inches of water; and it is positively asserted that in this operation there is no loss of silver; 6. The enriched lead from this furnace, containing from 7% to 12% of silver, is cupelled in the usual manner. Zinc of second quality is used, and in every case crude furnace-lead may be directly operated upon. Cast-iron pots, holding 10, 15, or 20 tons, may be employed; they last 8 or 10 months. The lead to be desilverized is melted, and heated a little beyond 411° C.; the zinc, in ingot, is placed upon the surface of the molten metal, when it immediately melts. The whole is stirred energetically by manual labour during 20 minutes, and afterwards left to cool at rest for 3 hours. The crust of zinc is taken off, and this process repeated twice. The crusts of zinc are liquated in a small pot, and the lead so drained off is transferred to the original pot. The average proportion of zinc of second quality required for the desilverization of very impure crude lead, containing 2000 grammes (65 ozs. 6 dwts. 16 grs.) of silver per ton (tonne = 1000 kilogrammes), is 1·6% of the market-lead obtained. The desilverized lead contains only from 5 to 6 grammes (3 dwts. 5 grs. to 3 dwts. 20 grs.) of silver per ton. The quantity of lead removed along with the crusts of zinc is from 1·75% to 2·25% of the lead under treatment. Although the manifold advantages ascribed to the so-called system of Flach may have been set forth from honest conviction, yet it is well to remember that they have proceeded from interested sources.

An attempt was made on a small scale in the chemical laboratory at Clausthal to dissolve out the zinc from the powdery argentiferous residues by dilute sulphuric acid, so as to facilitate the subsequent extraction of the silver from the residual product; but the result was abortive, for only about 12% of zinc was removed, and no silver passed into solution. The composition of the product after treatment by sulphuric acid was found to be as follows:—

Composition of Residual Product.

Lead	83·57
Silver	1·915
Copper	1·67
Zinc	9·32
Water	0·34
Sulphuric acid	1·11
Oxygen combined with lead estimated by difference ...	1·475
	100·000

It surely would have been preferable to use hydrochloric instead of sulphuric acid.

Produce and cost of desilverization by zinc at Clausthal.—The data afforded with respect to produce, by the desilverization of about 4000 ctrs. of lead at the Royal Silver Works at Clausthal, where the process has been in regular operation since the end of 1867, are shown in the table hereafter inserted (p. 167).

The lead operated upon contained 0·285% of copper,—0·003% of

iron,—0·442% of antimony,—and from 12 to 13 quints of silver per centner (1 quint = 5 grammes, and 1 centner = 50 kilogrammes). It was worked in charges of 250 centners each or about 12 tons. The first portion of zinc added was 260 lbs.,—the second 100 lbs., —and the third 40 lbs.,—total 400 lbs. Dezincification was effected with sulphate of lead and Stassfurth salt. The desilverized and dezincified lead was too hard and brittle to be fit for commerce. An attempt was made to soften it in the same manner as at Herbst's works, and it was kept melted in a Pattinson pot so long as 72 hours, yet without a satisfactory result. In order to remove the antimony still remaining, the lead was softened in a German cupellation-furnace with coal as the fuel, a charge of 180 centners being introduced. The Abstrich was allowed to flow out until litharge appeared, when the lead was tapped off and laded into pig-moulds. The lead was analysed before and after this treatment, and the results are as under :—

	Lead contained of foreign metals, per cent.	
	I. Before softening in the cupellation-furnace.	II. After softening in the cupellation-furnace.
Antimony	0·1963	0·0098
Copper	0·0062	0·0076
Iron	0·0037	0·0013
Zinc	0·0043	0·0026

The slags from the Pattinson pot, as well as those containing some lead from the dezincification of the poor lead, were smelted together in a litharge-reduction (blast) furnace, and the resulting lead was softened. The abstrich formed in the cupellation was very rich in antimony, and it is proposed to treat it for hard lead. The liquated lead after tapping held 3 quints of silver per centner, and, after skimming off the zinc scum, only 0·5 quint. This was for the most part put into the desilverizing-pot before the addition of the third portion of zinc ; and when this was not practicable it was desilverized by itself with 40 lbs. of zinc to 250 centners of lead. The rich argentiferous powdery zinc was smelted at Clausthal in a lead-regulus furnace with the addition of equal weights of lead-regulus and Oker copper-slags (the treatment will be fully described in the sequel), which are essentially composed of basic silicate of protoxide of iron; the silver passes into the reduced lead. Smelting was effected without difficulty at the lowest possible temperature, with a pillar of blast equal to 3 lines of mercury ; not much fume was emitted, and the mouth of the furnace was kept "dark." At the opening of the last condensing-chamber, which is connected with the stack, a wet sack was hung in order to catch as much fume as possible. After smelting during 36 hours only 0·1 pound of fume was collected, of which the content of silver was 1 quint per centner, so that there was no sensible loss of silver by volatilization. [Not the least value should be attached to a single experiment such as this.]

TABLE OF THE RESULTS OF DESILVERIZATION BY ZINC AT CLAUSTHAL.

	Silver.		Lead.		Percentage.	
	Pfd. (pounds).	Qt. (quint).	Ctr.	Pfd.	Silver.	Lead.
In the refined silver	463	33	...	...	95·635	...
In the market-lead	...	...	3403	37	...	85·038
In argentiferous intermediate products	16	97·45	309	62·5	3·503	7·711
In silver-free intermediate products	...	...	134	88·5	...	3·373
Total	480	30·45	3847	88	99·138	96·122
Loss	4	17·5	154	27	0·862	3·878
Pattinson's process—Loss	...	...	...	...	1·6	5 to 5½

1 centner = 50 kilogrammes. 1 quint = 5 grammes, or 0·005 kilogramme.

The conclusion at Clausthal was that in desilverization by zinc the loss both of silver and lead was less than in Pattinson's process.

The cost per centner of original lead is given as under:—

	Gr. (Groschen).	Pf. (pence).
Desilverization	8	7·861
Smelting argentiferous zinc	0	3·791
Cupellation	0	5·353
Softening poor lead	1	3·918
Reduction of litharge-slag from softening	0	9·562
	12	0·485

A trifle more than 1*s.* 2*d.*

Or in round numbers somewhat exceeding 23*s.* per ton.

1 Gr. = 1$\frac{1}{6}$*d.* sterling. 10 Pf. = 1 Gr.

One advantage of the zinc desilverization process, which is pointed out by Illig, is that lead which is too impure to be directly treated by Pattinson's process, and therefore requires preliminary purification by the softening process, is quite suitable for direct desilverization by zinc. But lead after having been desilverized by zinc must be softened; and it is much the same thing as to expense, whether softening takes place after or before desilverization. Another advantage is that zinc eliminates copper from lead, which Pattinson's process does not in a sensible degree. A third advantage is that it needs only about one fourth of the number of workmen required in Pattinson's process. The special disadvantage of the process is the difficulty of treating the highly zinciferous slags produced in the operation of dezincifying the poor lead and of smelting the powdery argentiferous zinc skimmings.

Dezincification of desilverized lead by superheated steam.—This process is stated to have been invented by Cordurié of Toulouse, and was patented in England, December 13, 1866, about three weeks before

the date of Flach's patent.[8] Lead to be desilverized is treated in the usual manner with the addition of 2% of zinc. After the removal of the crust of argentiferous zinc containing some lead, superheated steam is passed into the desilverized molten lead, whereby the zinc retained by the latter is oxidized by the oxygen of the steam with an equivalent evolution of hydrogen, while the lead is but slightly attacked. The oxide of zinc so formed rises to the surface in the state of powder, and is skimmed off. The hydrogen, which may carry along with it some oxide of zinc, is passed through a suitable condensing-chamber, in order that this oxide may be deposited and collected. The argentiferous crusts of zinc are to be exposed to the action of a current of hot air, "in the midst of the melted alloy," with a view to the oxidation of the zinc; or, preferably, to that of a jet of superheated steam under the necessary pressure. The zinc is thus oxidized together with a certain quantity of lead, and the mixed oxides are to be separated from the molten argentiferous lead by skimming or liquation. The argentiferous lead, after this treatment, is cupelled, and "the oxides are regenerated; but they are previously made to traverse a bath of lead, to which they yield up any silver which they may have drawn off with them, as well as traces of oxide of lead."

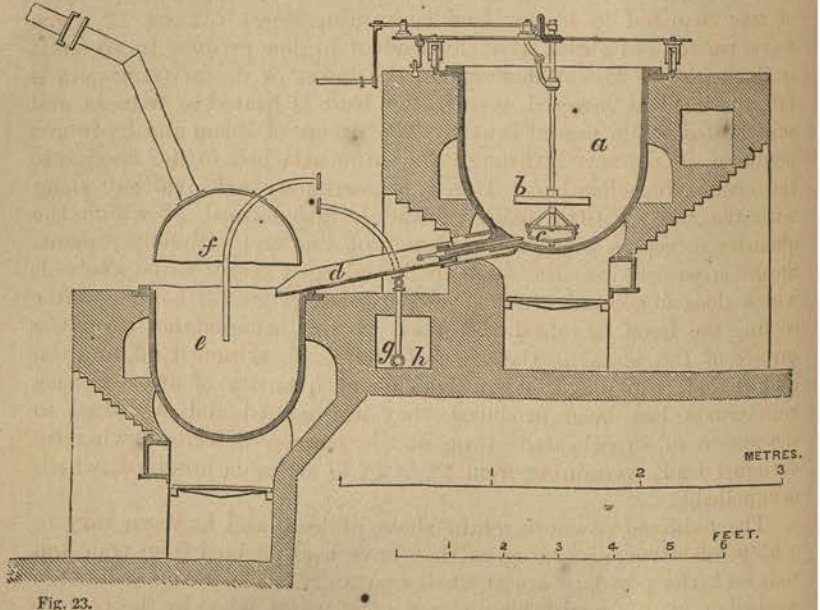

Fig. 23.

a. Cast-iron pot for mixing.
b. Agitator in the form of helix.
c. Perforated box of sheet-iron containing the charge of zinc.
d. Spout for tapping off the desilverized lead.
e. Cast-iron pot in which the desilverized lead is dezincified.
f. Cover or hood communicating with the condensing-chamber by means of a pipe.
g. Pipe for conveying superheated steam.
h. Flue, in which the steam is superheated.

[8] Improvements in the treatment of lead and argentiferous litharge.

A description of Cordurié's process, as practised at Messrs. Rothschild's works at Havre, has been published by Gruner, and from that the following information has been extracted.[9] The apparatus employed is represented in the annexed woodcut, which is copied from the engraving given by Gruner.

There are two pots to receive the desilverized lead which are used alternately; and there are, consequently, two openings in the mixing-pot communicating with the receiving-pots respectively, each of which openings is provided with a plug arrangement. The charge of zinc is placed in a perforated box, and so gradually rises as it melts through the bath of lead; and mixture is promoted by causing the vertical shaft carrying this box and the agitator to rotate. The mode of communicating rotation to the agitator and box containing the charge of zinc, will be sufficiently intelligible without reference-letters; the whole system is placed upon a little carriage revolving on rails. Shortly after the fusion of the zinc the rotating part of the apparatus is removed, after which the bath is well stirred by hand for a few minutes. The argentiferous crusts are transferred to a small pot close by and there liquated, the lead which drains off being put back into the original mixing-pot. Usually the same lead is thus treated three times successively with zinc. The total quantity of zinc required is 1% for lead containing 0·001 (32 ozs. 13 dwts. 8 grs. per ton) of silver; but for lead of higher produce in silver it is from 1·5% to 2%. When one of the lower or dezincifying-pots is full, the hood is lowered over it, the lead is heated to redness, and superheated steam passed into it. The excess of steam and hydrogen produced is conveyed through the pipe attached to the hood into the condensing-chamber. Iron and antimony are oxidized along with the zinc; a little oxide of lead is also formed, of which the quantity increases with the proportion of zinc and antimony present. Steam is passed into the lead until hydrogen ceases to be evolved, which does not occur until after the lapse of 2 or 3 hours. After cooling the hood is raised, the oxide of zinc accumulated upon the surface of the metal in the state of powder is skimmed off, and the lead is cast into pigs. When a sufficient quantity of argentiferous zinc crusts has been produced, they are melted and subjected to the action of superheated steam in the manner described, whereby enriched lead, containing from 1% to 2% of silver is obtained, which is cupelled.

The oxidized powders retain shots of lead, and as these vary in content of silver, according as they have been derived from poor and rich lead, the powders are treated separately. The *poor* powders are washed on an inclined table under a jet of water, whereby the powder is carried away and the shots of metal left, which are melted in a reverberatory furnace, or added to the original poor lead in the mixing-pot. The powders collected by levigation are of three kinds:

[9] Ann. des Mines. 6 sér. 13. p. 395. 1868.

the heaviest consists of oxide of lead with but little zinc, and it is reduced in a reverberatory furnace; the middle portion consists of the oxides of lead and zinc, which is washed again with the addition of fresh powders; and the lightest portion may be sold as oxide of zinc. The *rich* powders are finely-sifted in a vat of water; and the shots and plates which remain on the sieve are added to the rich lead, while the oxides and fine metallic particles deposited in the vat are treated by cold hydrochloric acid of sp. gr. 1088. The oxide of zinc is dissolved, and the resulting chloride of zinc is thrown away; the insoluble residue consists of the chloride of lead and silver, of oxychloride of antimony, and of fine metallic particles. This residue is drained, and then melted in a cast-iron pot. The metallic particles collect at the bottom and constitute rich lead. The melted chloride is skimmed off and reduced in a reverberatory furnace with admixture of lime and carbonaceous matter; and the lead thus yielded, which contains but little silver, is returned to the mixing-pot.

The market-lead is said to be completely free from zinc and copper. The desilverized zinciferous lead at the works at Havre contained 0·75% of zinc; but, after having been subjected to the action of steam, it yielded only feeble traces of zinc. The powder collected on the desilverized and dezincified lead consisted of 79% of shots of *poor* lead and 21% of oxides, in which were found 61·4% of oxide of lead and 30·8% of oxide of zinc, the residue consisting of "iron, carbonic acid, etc.," but no antimony was detected in it. The oxides derived from the rich plumbo-zinciferous crusts being more impure are treated with hydrochloric acid. The most impure product is deposited in metallic plates on the interior of the hood when the rich crusts are operated upon. The boiling caused by the steam projects continually metallic particles against the hood, where they flatten and stick; they are returned to the mixing-pot.

Formerly, at this establishment, 250 tons of lead were treated every month by Pattinson's process, or 10 tons in 24 hours. From 50 to 52 men were employed, and the coal consumed amounted to from 45% to 50% of the weight of the lead. The loss upon the lead of Carthagena was 6%, and 4% on "pure lead." At present (1868), with only two mixing-pots and two receiving-pots containing 10 tons each, 20 tons are treated in 24 hours, or 500 tons per month; and only 23 men are employed, inclusive of those engaged in all the accessory operations. The loss upon pure lead is 1% instead of 4%, and the consumption of coal 10% instead of from 45% to 50%. It is added that the work is not so hard as that of Pattinson's process, there is less dependence on the caprice of the workmen, and the lead is very pure. Every day 90% of market-lead is produced, whereas formerly, in Pattinson's process, in order to obtain 10 tons of market-lead, it was necessary to have six pots in operation, containing altogether from 60 to 70 tons of lead. The cost of the zinc process for the kinds of lead usually treated at this establishment is stated to be 25 francs (20s.)

per ton, instead of 55 francs (£2 4*s*.). The yield of silver is stated to be under 2% of the total indicated by assay, and the loss of lead less than 1%. However, in an example given, the loss amounted to 3%.

Hochstätter informs me, that on visiting lead-smelting works at Mechernich (Commern), in September, 1869, he found Cordurié's process in operation, and that not less than from 15% to 17% of the lead was converted into scum.

Gruner concludes with the prediction that the Cordurié process will shortly supersede every other method of desilverization. I venture to prophesy the contrary. If it be a fact,—as it is,—that the zinc can be quickly and economically separated from lead desilverized in Parkes' process, by the usual and simple method of softening, hereafter to be described, it is not likely that the agency of superheated steam will be adopted instead of that method.

Later trials of Parkes' process in Prussia.—The method of desilverizing with zinc has been subjected to further modifications in the Prussian smelting works in the Harz and Silesia, which have been recently described by Messrs. Wedding and Braüning.[10] These will now be briefly noticed in order to complete the account of the working of the process.

In order to economise zinc, the practice has been adopted in Silesia, where the lead is nearly free from copper, of commencing the desilverizing with the second and third zinc-skimmings obtained from the previous charge, adding only a small proportion of fresh zinc, instead of working entirely with the latter. In this way the quantity of zinc used has been reduced from 1·48% to about 1%. In the Upper Harz it was not found possible to carry the saving so far, as it was discovered that the copper separated had a tendency to go back into the lead, in such proportion that it could not afterwards be removed in the process of softening.

The method of refining the impoverished lead with Stassfurth potash salts, and subsequent softening in a cupellation-furnace, proved to be objectionable, from causing considerable loss both of time and materials. The method of simply poling the lead at a high temperature was therefore adopted, whereby the foreign metals are oxidized, the zinc being removed before the antimony, the latter as antimoniate of protoxide of lead (*Abstrich*). Not much lead is oxidized until after the separation of the antimony.

In the above process the steam given off by the green wood used in poling, owing to the high temperature of the metallic bath, is decomposed by contact with the zinc, producing oxide of zinc and hydrogen, lead under these circumstances being only slightly acted upon. It is, in fact, substantially the same in principle as Cordurié's process described at p. 167. A charge of 180 ctrs. of lead, containing 0·7% of zinc and up to 1% of antimony, may be completely refined by poling for 10 hours at a cherry-red heat. The removal of the zinc requires

[10] Zeitschrift für das Berg-, Hütten- u. Salinenwesen, 17. p. 231 et seq. 1869.

about 6 hours, and the antimony from 3 to 4 hours more. The refined lead contains at a maximum not more than 0·006%, either of zinc or antimony. The yield of best-refined lead is from 74% to 76%, and the loss does not exceed 1%. The fuel consumed is about 10% of the weight of the charge, against 14% used in the former method of refining.

The use of other oxidizing agents at a lower temperature, such as nitrate of soda, in the same manner as recommended for the refining of iron in Heaton's process, has been tried; but the results were unfavourable, as the lead was oxidized to a considerable extent, as well as the zinc and antimony. Similar results were obtained by the use of hot-blast at a dull red-heat.

At Braubach, on the Rhine, dezincification of the lead has been advantageously effected by treating it with litharge in a reverberatory furnace at the melting-point of litharge. The same plan was tried in the Harz, below the melting-point of litharge, but without effect; and the dust of litharge was injurious to the health of the workmen, owing to the operation being conducted in open vessels.

A great number of experiments has been made with a view to dispense with the blast-furnace in the treatment of the argentiferous zinc—a treatment which must assuredly occasion much loss of silver; but none were successful, until the introduction of the steam process. Among the latest of these experiments may be mentioned the attempt to remove the silver by treatment with litharge in a reverberatory or cupellation-furnace. The zinc skimmings were covered with an equal weight of litharge, and subjected to a long-continued heat, with the intention of oxidizing the zinc by the direct action of protoxide of lead, and concentrating the silver in the reduced lead. It was, however, found that as soon as the zinc became exposed to the air after the protecting cover of litharge was removed, it took fire and burnt with the production of oxide of zinc, which carried off a large quantity of silver. The fusion went on very slowly, and it required 12 hours of strong firing to liquefy the charge, and even then a quantity of infusible alloy remained on the surface. As soon as the whole of the zinc had been separated, whether by the action of the litharge or of the atmosphere, and the charge had been subjected to the highest attainable temperature for 4 or 6 hours, the surface was skimmed and an *Abzug* obtained, which amounted to 42% of the charge, and was full of shots of rich lead, containing from ½% to 1% of silver. The cupellation of the residual lead went on in the regular way, and produced rich litharge to the extent of 39% of the original charge, and containing 0·0075% of silver. The loss from volatilization was very large, the fume from the litharge-channel (see description in the sequel of the German cupellation-furnace) containing 0·06%, and that from the chimney 0·01% silver. The results obtained, when the process was tried in open pots or in reverberatory furnaces, were equally unfavourable, the infusible residues forming from ¼ to ⅓ of the weight of the charge, and containing from 2% to 3% of silver.

At Lautenthal, Cordurié's process has been adopted, and is sup-

posed to possess some small advantages over simple poling, although the cost is said to be nearly the same in both. The advantages claimed are the smaller proportion of oxidized matters, the production of an oxide of zinc suitable for paint, and less injury from fume to the health of the workmen consequent on the use of covered pots.

The general manipulation is similar to that already described as in use at Havre, with the following slight modifications. The desilverization and dezincification of the lead are performed in the same pot, one of a series formerly used for Pattinsonizing, which has been adapted to the new process by the addition of a moveable hood. The charge is 250 ctrs., and steam of 15 lbs. pressure, instead of from 60 to 75 lbs. as at Havre, is passed into the metal at a cherry-red heat during 3 hours, whereby the zinc is said to be separated. The crust of oxide is then removed, and the steaming is continued for about an hour more with access of air, which is admitted through holes in the hood specially adapted for the purpose. In this way the antimony is said to be entirely removed, as a black melted *Abstrich*, in the same manner as in poling. But antimony does not communicate blackness to *Abstrich*, as will be shewn hereafter.

The argentiferous zinc crusts are liquated at a comparatively low temperature, in order, in the subsequent treatment with steam, to prevent the formation of the rich oxides, which are found to result from draining the zinc too dry at first. The oxides obtained from the dezincification of the desilverized lead are washed upon an inclined frame as at Havre; but the subsequent treatment with hydrochloric acid is omitted. The products consist chiefly of plumbiferous residues, with 85% of lead, which are revived, and a smaller quantity of finely-divided oxide of lead and zinc, of a yellowish colour, not unsuitable for paint. The oxidation of the argentiferous zinc is effected by steam in the same manner. There is danger in this part of the process, owing to the large quantity of hydrogen produced, which may cause explosion if air is incautiously admitted. In order to prevent this, it is desirable to have a second steam jet blowing into the hood, so that the hydrogen may be discharged into an atmosphere of steam. Owing to the large amount (55%) of lead left in the zinc crusts at Lautenthal, the oxide of zinc formed is poorer in silver than the enriched lead, the latter containing from $1\frac{1}{2}$% to $1\frac{3}{4}$%, and the former from $\frac{1}{2}$% to 1% of silver. At Havre, where the zinc is taken off drier, reverse conditions prevail. In the Harz the yield per 100 ctrs. of zinc, containing $1\frac{1}{2}$% of silver, is from 70 to 75 ctrs. of enriched lead, and from 32 to 26 ctrs. of oxides.

The treatment of the rich oxides with hydrochloric acid has not been adopted at Lautenthal on account of the cost of the acid; and they are treated in the same manner as rich silver ores, being added to the lead in the cupellation-furnace. In order to prevent the dry powdery oxide from being blown away, the blast is stopped until a pasty mass is formed on the surface of the lead, when it is then let on, and the fire urged until an imperfectly melted slag or *Abzug* is formed, which is drawn off in the usual way. This *Abzug* does not contain more than

1500 grammes of silver in the ton, so that most of the latter metal goes over to the lead.

The Andreasberg slag-lead, which is extremely impure, containing large quantities of antimony and copper, and about 0·06% of silver, has been experimentally treated by the above process with, it is said, favourable results. It is, however, necessary to remove the greater part of the antimony before desilverizing. On melting down the charge of 200 ctrs. an *Abzug* is formed, containing about 10% of copper, which is removed, and steam is afterwards passed through during 16 hours, so as to convert the antimony into *Abstrich*. The desilverizing is then effected by zinc, a somewhat larger quantity (1·42%) being used than with the lead from the other Harz ores. The following is said to be the composition of lead so refined:—

Copper	0·00476
Antimony	0·00317
Iron	0·00166
Zinc	0·00265
Silver	0·00060
Lead	99·98716
	100·00000

It is reported that by cautiously adding zinc to lead in successive portions, copper, gold, and silver may be removed separately and in the order indicated. The experiments on this subject are however not concluded. Gruner, on the contrary, states that at Braubach it is found that gold is first removed, then copper, and lastly silver.[11]

More space has probably been devoted to these alleged improvements of Parkes' process than they deserve. Yet it is instructive to note how metallurgical processes may be approved one year and condemned the next in the same journal. The reader should hence learn a lesson of caution with respect to conclusions hastily arrived at, even by practical men, concerning new processes. Much experience has of late been obtained in the practice of that process in England; and the results are diametrically opposed to many of those above recorded. I am informed that one of these chloride processes was offered to a British lead-smelting firm for 40,000*l*.,—a firm, which, it so happened, had had great experience of Parkes' process, and which found no difficulty in profitably separating zinc from lead without the aid of chlorides. Even in these days, 40,000*l*. was an outrageous price to ask for such a process, except perhaps of a Limited Liability Company!

DECOPPERIZATION OF LEAD BY ZINC.

The separation of copper from lead by this process has been carried to a successful practical issue by Mr. W. Baker, whoever may claim to have originated the suggestion; and I have pleasure in commu-

[11] Ann. d. Mines. 6. sér. 13. p. 393. 1868.

nicating the following description (Feb. 1868) of the process by Mr. Baker himself.

When a certain proportion of zinc is melted with lead containing copper and then cooled, a lead-zinc alloy is formed which withdraws most of the copper from the lead, and which can be removed as it floats on the surface of the melted metal in a pasty or semi-solid condition. This alloy is stated to be definite in its character; for, if it be melted with an equal weight of lead or zinc, the same weight can be recovered by liquation. In the first case the lead withdraws 0·026% of copper and 0·379% of zinc. In the case of melting the alloy with zinc and separating again by liquation, the zinc is recovered containing 1·98% of lead and 0·354% of copper.

The proportion of copper in the zinc alloy depends upon the quantity originally contained in the lead and the amount of zinc used in the decopperizing operation; on the other hand, the quantity left in the decopperized lead when ½% of zinc has been employed is very constant, and may be estimated at about 1 oz. per ton. In operating upon nearly 100 tons of lead, which contained from 10 to 15 ozs. of copper per ton, the copper was reduced on the average to 1 oz. 21 grs. per ton, *i.e.*, 0·0033%. The same result can be got if the lead contain as much as 0·06% of copper (20 ozs. per ton), a proportion seldom exceeded in "soft" lead of commerce. When the process is carried on with skill only 0·0013% of copper is left in the lead.

The operation is conducted in the following manner. Five tons of lead are melted, skimmed, and kept sufficiently hot to prevent the metal setting at the sides of the pot. Twenty-eight pounds of zinc are melted with about 2 cwts. of lead in a small pot adjacent. This pot already contains about 14 lbs. of zinc together with some lead from a previous operation. When quite liquid more lead is added from the larger pot, in order to dilute the alloy before mixing with the entire charge. The contents of the small pot, which should be hot enough to prevent any alloy separating, are then added to the charge and stirred well into the melted metal. The fire is now withdrawn and the whole allowed to cool down. In a short time a pasty alloy rises to the surface and is removed by a perforated skimmer into the small pot. This operation is continued until the lead begins to set at the sides of the pan. The charge must then be re-heated, and the alloy in the small pot liquated by heating at a regulated temperature, which will permit of the zinc alloy being removed from a quantity of zinciferous lead, which will be left with only a trace of copper. Fourteen pounds more zinc are now melted with this residue in the small pot, and the operation is repeated. More certain results are obtained by thus adding the zinc in two portions. Finally all the zinc dross and alloy are liquated in the small pot. The quantity of alloy obtained is about 1 cwt. This will contain about 25% of zinc or 28 lbs. of the zinc employed for one operation. It may be estimated that 14 lbs. will be left in the decopperized lead and 14 lbs. also in the liquated product remaining in the small pot ready for the next operation.

The zinc remaining in the decopperized lead is oxidized in a reverberatory furnace with a slag bottom, or in a pan such as is used in the furnaces for softening hard lead. (See p. 459.) In a round pan containing from 8 to 10 tons, set in a furnace of the latter description, a charge was worked off in about 30 hours including charging and tapping out. From 90 tons an average of 95% of softened lead was obtained. The dross was easily reduced and yielded ordinary soft lead.

The zinc alloy containing copper and also most of the silver is best economised by melting down in a small-blast furnace when a rich argentiferous lead may be obtained.

The first experiment upon a large scale was made May, 1861, and the results of thus decopperizing slag-lead of Derbyshire, and specimens of the white-lead produced from the lead so treated, were exhibited by Messrs. Rawson, Barker, and Co., at the International Exhibition of 1862:—

	Contained per cent.			
	Copper.	Zinc.	Silver.	Iron.
1. Lead before adding zinc	0·0642	—	?	0·0294
2. After taking off zinc alloy	0·0083	0·376	trace	0·0402
3. After oxidation of the zinc	0·0071	—	?	0·0129
4. Liquated product from zinc alloy	0·0948	0·337	0·007	0·0490
5. After distilling off zinc from the alloy	0·2097	—	0·0268	0·0071

The proportion of zinc left in Nos. 2 and 4 is interesting, as in the former a much larger quantity of lead was present. The iron estimations are not worth much. In working upon the large quantities of lead (2000 grains) the quantity of solution is likely to add to the proportion of iron. In one case Baker detected in the ordinary quantity of distilled water and reagents used as much as 0·002% of iron to the 2000 grains of lead.

At the works in Germany, where desilverization of argentiferous lead by zinc has been conducted and the zinc has been added in successive portions, observations have been made concerning the elimination of other metals along with silver. The following results have been obtained by Illig:—

		In the lead after addition of zinc and removal of zinc crusts.		
Metals per cent.	In the original lead.	After 1st portion.	After 2nd portion.	After 3rd portion.
Antimony	0·035	0·034	0·048	0·046
Copper	0·161	0·003	0·007	0·008
Iron	0·005	0·006	0·003	0·004
Zinc	0·006	0·227	0·541	0·777
Silver	0·0283	0·021	0·005	0·0062

Illig is puzzled to account for the increase in the proportion of copper after the second and third additions of zinc, except on the supposition, by no means unreasonable, of errors in the analysis, connected with the determination of such minute proportions of foreign substances in large quantities of lead.

REFINING OR CUPELLATION.

This interesting and truly venerable metallurgical process is clearly indicated in the Old Testament, and seems to have been a favourite illustration with the Jewish poets. The most striking reference to it is, in my opinion, the following from the Book of Jeremiah:[1] "The bellows are burned, the lead is consumed of the fire; the founder melteth in vain: for the wicked are not plucked away. Reprobate (or refuse) silver shall men call them, because the Lord hath rejected them." In this passage all the essential points are mentioned, the artificial blast, the oxidation or consumption of the lead, and the "reprobate silver," silver dross, or litharge. There is either no residue of precious metal, or what remains is contaminated with impurities so tenaciously adherent as not to admit of being separated by the oxidizing and solvent action of molten litharge.

The principle of the process of refining or cupelling may be perfectly illustrated by experiments with the blowpipe. Let the oxidizing point of the blowpipe flame be directed upon a piece of lead about as large as a small pea, contained in a little thin capsule of burnt fire-clay, made as non-absorbent as possible to melted litharge, when a stratum of liquid protoxide of lead or litharge will be quickly formed, and after blowing for a few minutes the whole or greater part of the lead will be oxidized. The substance of the capsule which had been in contact with the molten litharge will be found to be sensibly corroded. Let a bit of tin or other easily oxidizable metal be thus treated, of which the resulting oxide is infusible *per se*, then oxide of tin or of the other metal will be left in the capsule, presenting, it may be, a somewhat scoriaceous aspect; but if the experiment be repeated with the addition of a certain quantity of lead, then the product will be wholly liquefied, the infusible oxide combining with, or dissolving in, the molten litharge. Now let another experiment, similar to the last recorded, be made with the addition of silver, then, if the blowing be continued long enough, the product will consist of molten oxide of lead containing oxide of tin or other oxide, and of a globule of silver, which, after cooling, will admit of being easily detached from the oxidized mass. Silver is not oxidized by atmospheric air when heated to a degree far beyond its melting-point, either alone or in contact with such a highly oxidizing agent as litharge; whereas, under these conditions, various metals are quickly converted into oxides which dissolve in molten oxide of lead. Hence, it is obvious, that lead may not only be separated from silver by the joint action of atmospheric air and heat, but may also be used as a means of separating other metals from silver. The operation above described is technically termed scorification. What is thus done on a diminutive scale may be and is equally well done on a great scale, substituting a reverberatory

[1] Ch. vi. *v.* 29, 30.

furnace having a concave shallow bed of suitable refractory material for the capsule, and continuous blast produced by machinery for the blowpipe; but, as on the great scale it is necessary to oxidize a very large quantity of lead to obtain comparatively little silver, a contrivance must be adopted for allowing the molten litharge to flow off instead of accumulating on the furnace-bottom, and for supplying *pari passu* fresh lead for oxidation.

Instead of heating lead before the blowpipe in a fire-clay capsule, which is practically non-absorbent to, though it may be somewhat corroded by, molten litharge, let the experiment be made with a little shallow cup-shaped vessel, called a cupel, composed of the white powder of calcined bones, commonly termed bone-ash, duly tempered with water, fashioned in a suitable mould by compression so as to be rendered solid, and afterwards thoroughly dried. A vessel of this kind is not corroded by litharge at a high temperature, but instantly absorbs it when melted, just as blotting paper absorbs water. Hence, by performing the experiments previously recorded in such vessels, the silver is left as a globule in the cavity, all the lead passing into the substance of the cupel, and, in the event of the presence of other metals, carrying them along with it after their conversion into oxides. It should, however, be stated that the oxides of certain metals, such as tin and nickel, need so much molten oxide of lead for their complete liquefaction, that, in consequence of its rapid infiltration, sufficient oxide of lead for that purpose can never be accumulated on the cupel. In such cases, it would be necessary to resort, at least as a preliminary step, to the first-mentioned process of scorification. Although on the small scale, as in assaying, it is convenient to cause total removal of the oxide of lead by absorption, yet on the great scale it would not be possible to conduct the process of cupellation on this principle on account of the large quantity of bone-earth that would be required; and a test bottom of sufficient thickness to absorb all the litharge produced would be so thick as to make it very difficult, if not impossible, to keep it hot enough throughout to prevent the solidification of the oxide in its substance, when infiltration would immediately cease. Absorption of oxide of lead can only take place along the walls of the cupel, and in the case of very large cupels, like the test, the absorbing surface would be very small relatively to that of the bulk of lead. However, there is no better material than bone-ash for a test-bottom, not, let it be borne in mind, because it is absorbent, but solely because it resists satisfactorily the corrosive action of molten litharge.

English Cupellation.

Description of the furnace and test. — These are represented in the annexed woodcuts, figs. 24 to 29, prepared from drawings by Mr. Bowen of the cupelling-furnaces in operation at the Llanelly Lead Works in 1859, for which I am indebted to Mr. Charles and Mr. William Nevill. The fire-place, it will be noted, is large compared with the body of the furnace, which is short. The space between the fire-bridge wall, *a*, and the flue-wall, *h*, is entirely open from front to

back, where it should be closed by iron doors to prevent too much loss of heat; and in these walls are securely fixed two wrought-iron bars, *i*, *i*. At *b*, *b*, are shown two bars of wrought-iron, upon which rests the oval ring, termed compass-ring, of wrought-iron, *m*, *m*, made in two equal and similar parts, each having two projecting pieces to serve as

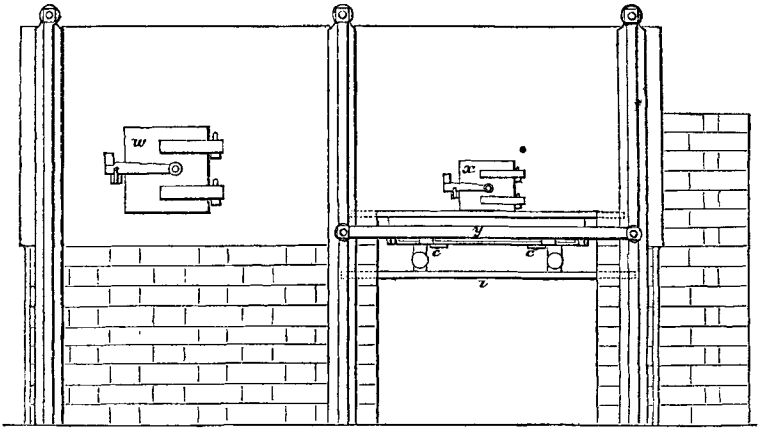

Fig. 24. Front elevation.

supports. The ends of this ring are supported by *b*, *b*; the upper surface of it is covered with brickwork plastered over with fire-clay, which entirely surrounds its inner edge except at the front end, where an opening is left. There is a downward flue, *z*, which com-

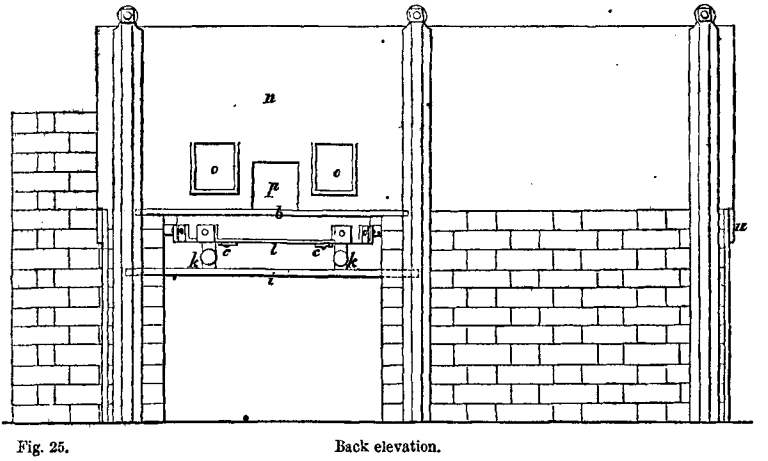

Fig. 25. Back elevation.

municates with the body of the furnace by two openings, as shown in figs. 26, 28, and with a high stack by a long underground culvert. At *p* is an opening in the back of the furnace through which passes a blast-pipe; and on each side of *p*, is an opening, *o*, through which pigs of lead are inserted, and gradually pushed forwards as they melt away, thus

providing a continuous supply of fresh lead to the test: these openings are in a plate of cast-iron, *n*, which covers the whole of the upper half of the back. At the front is a similiar plate of cast-iron, *u*, having a fire-door, *w*, and a door, *x*, contiguous to the breast of the test, where the molten litharge flows over; and below *x* is a cross-bar of

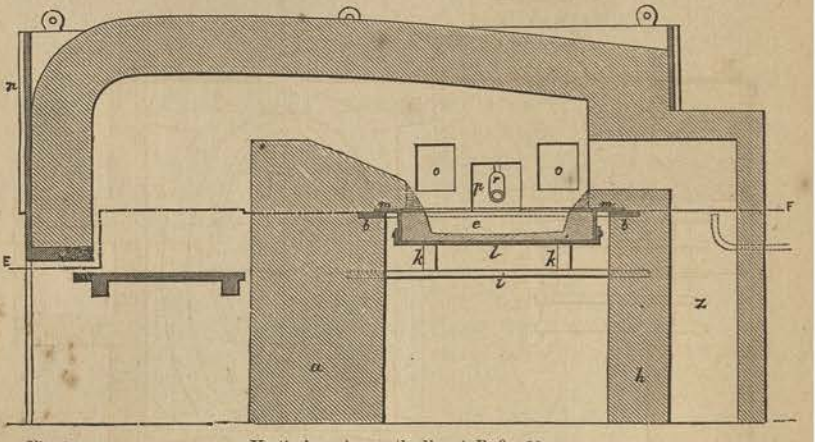

Fig. 26. Vertical section on the line A B, fig. 28.

wrought-iron, *y*, termed skimming-bar, which serves as a fulcrum for tools. The dotted line above *z*, fig. 26, represents a steam-jet in a flue leading to a condensing-chamber, through which the fume from the cupellation-furnaces must pass in its course to the stack.

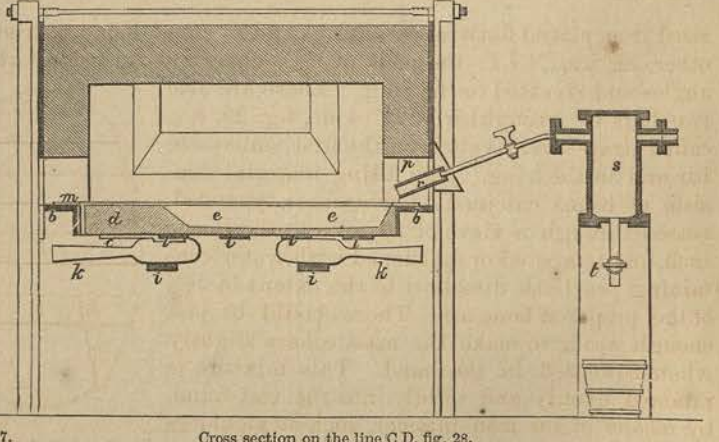

Fig. 27. Cross section on the line C D, fig. 28.

The test consists of a frame of wrought-iron, filled in with bone-ash. It is shown in longitudinal section fig. 27, *d*, *e*, *e*, in cross section fig. 26, in plan fig. 28, and bottom upwards fig. 29. The frame is an elliptical ring, made of a flat wrought-iron bar, $4\frac{1}{2}''$ wide and $\frac{1}{2}''$ thick, having a bottom formed of four transverse bars of the same

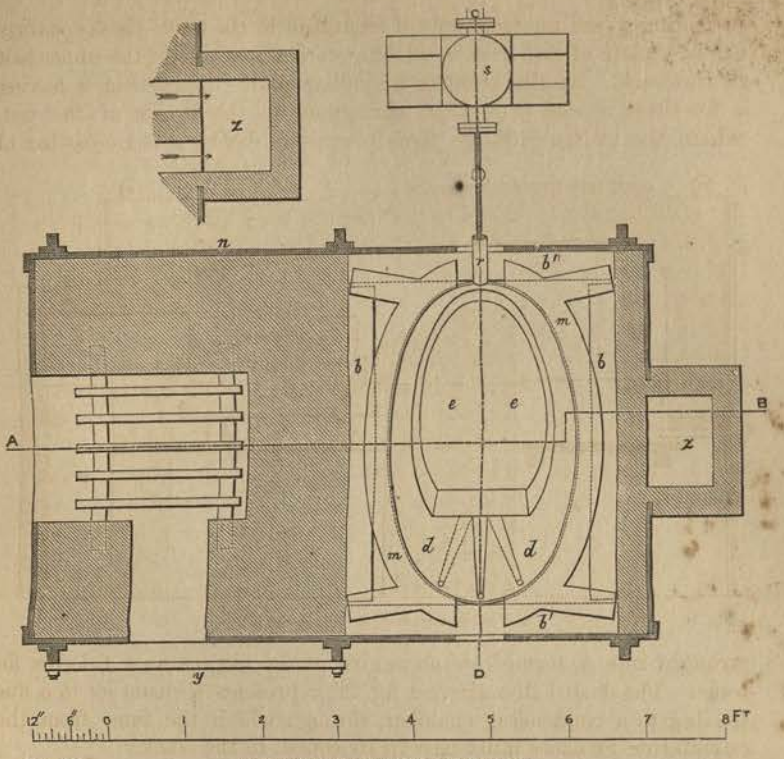

Fig. 28. Horizontal section on the line E F, fig. 26.

sized iron, placed flatwise parallel to, and at equal distances from, each other, fig. 29, *l*, *l*, *l*, *l*; the ends of these bars are turned up at right angles and rivetted to the ring.[2] There are also two bars of wrought-iron $2\frac{1}{4}''$ wide, fig. 29, *c*, *c*, called strap-bars, rivetted on the first transverse bar and on the ring. The filling material consists of bones calcined to whiteness, pounded, passed through a sieve of 26 holes to the linear inch, and tempered or moistened with water containing pearl-ash dissolved to the extent of $2\frac{1}{4}\%$ of the prepared bone-ash. There should be just enough water to make the mass cohere slightly when squeezed in the hand. This mixture is rammed evenly and solidly into the test-frame by means of an iron rammer, such as moulders use in filling moulds with sand, so as completely to fill it and leave the upper surface level. A cavity, *e*, *e*, is then scooped out, of the shape and depth

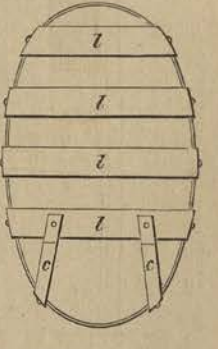

Fig. 29. Test, shown with the bottom upwards.

[2] According to Pattinson, the ends of these bars should be rivetted on the *inner* side of the ring, and be exactly on a level with the lower edge of that ring, so that when the test-frame is filled it may lie solidly on the floor.

shown in the woodcuts, for which purpose a little trowel is employed. The bottom should incline about $\frac{1}{4}''$ towards a point exactly midway between the opposite sides of the ring and the second and third cross-bars, so that by drilling a hole at that point every particle of liquid metal in the test may be drawn off. It will be perceived that between the flat end of the cavity in the test, and the ring at that end, the distance is 13″: this part, *d*, is called the breast of the test. At the same end of the ring the bone-earth was formerly cut entirely out, thus leaving a narrow channel bounded on one side by the iron of the ring, and on the other by a vertical wall of bone-earth; but a round hole is now substituted. A channel about 2″ wide at the inner end, 1″ at the other, and $\frac{1}{8}''$ deep, is cut in the surface of the breast extending from the middle of the cavity at the breast end to the hole through that end of the test, so that molten litharge may thereby flow over the breast and thence downwards into a cast-iron pot placed underneath to receive it. There is no contact between the litharge and the iron of the ring. In process of working, this groove becomes too deep on account of corrosion, and must then be stopped by a plug of tempered bone-ash. A second and similar channel must next be made where indicated by dotted lines, and when this in its turn has become too much corroded downwards, it also must be stopped, when a third groove also indicated by dotted lines must be made. When this groove becomes in like manner too much corroded, the test itself will be no longer serviceable, or it will be filled with silver which must be left to solidify. When sufficiently cold the test is removed and the cake of silver detached. The test-frame must be quite emptied preparatory to refilling. The test being thus prepared is left slowly and completely to dry before use. A test of the dimensions given will require about $2\frac{1}{2}$ cwts. of dry bone-ash, and will hold about 8300 ozs. of silver. The bones are burned in an arched kiln, which is employed also for burning fire-bricks at the Llanelly Works. I have given the precise dimensions of one of several tests which I measured at the Works; but it is hardly necessary to remark, that those dimensions and the particular arrangement of the cross-bars are not rigidly adhered to. The use of strap-bars is exceptional.

The blast is produced by a steam-jet [*i.e.* at these works, but it is usually produced by a fan], conveyed by a pipe $\frac{3}{4}''$ in diameter from a circular steam-chest, *s*, supplied with steam at 26 lbs. pressure to the inch; the free end of this pipe is reduced to $\frac{1}{8}''$ in diameter in the clear. The blast-pipe is shown at *r*, and is inclined so that the blast may strike the middle of the second cross-bar on the left, in fig. 27; it is of iron, circular, $1\frac{1}{2}''$ in internal diameter, and $\frac{1}{2}''$ thick. In the upper end of the blast-pipe the reduced end of the steam-pipe is fixed axially and projecting not more than $\frac{1}{2}''$ inwards. A considerable space is thus left round the end of the steam-pipe, through which the external air rushes when the steam is let on. At *t* is a stop-cock for drawing off the water resulting from the condensation of steam in the steam-chest, *s*.

The test being thoroughly dry is brought up close against the under side of the compass-ring, *m*, *m*, some of the bone-ash material mixed with water to the consistency of paste having been previously plastered round its outer border on the top side in order to act as luting; and as the test-ring is somewhat larger than this ring, it is overlapped by the latter. In this position the test is fixed firmly by the insertion of four iron wedges, two of which are shown at *k*, *k*, between the bottom of the test-frame and the transverse bars, *i*, *i*.

Mode of conducting the process.—A new thoroughly dried test having been fixed in its place in the manner described, the fire is lighted, and the heat very gradually raised to bright redness—say, to a temperature above the melting-point of litharge, but considerably below that of silver—when molten lead is introduced sufficient nearly to fill the cavity. The lead is added molten in order to save time and not to cool the test; and for this purpose there should be a suitable cast-iron melting-pot attached to the furnace. As soon as the temperature has risen to the melting-point of litharge the blast is let on. Oxidation proceeds regularly and the molten litharge on the surface of the lead is blown towards the breast where it flows through a channel previously cut in that part and drops into the pot shown in fig. 30. A constant supply of fresh lead is kept up by gradually protruding pigs through the two openings *o*, *o*, at the back. As soon as the litharge-pot is full, it is wheeled away, and another is substituted, and so on in succession. When the litharge in a pot is solidified, it is turned out in a cake; and as it cools it swells up, exfoliates, and falls to pieces. The process is thus carried on until the lead in the test has become enriched, say from 200 to 250 ozs. of silver in the ton to 3000 ozs. in the ton, when it is tapped out into the large cast-iron pot fig. 31, by drilling a hole in the bottom of the test, where stated in the foregoing description of the test, and cast into pigs. After

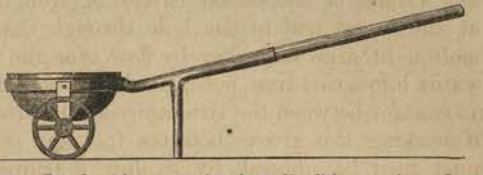

Fig. 30. Pot of cast-iron to receive the molten litharge as it overflows.

Fig. 31. Pot of cast-iron for receiving concentrated lead tapped off at the bottom of the test.

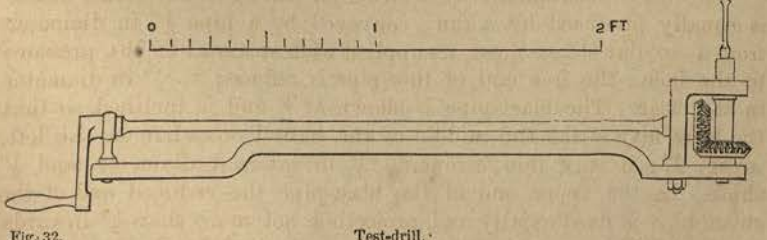

Fig. 32. Test-drill.

tapping, the hole is plugged up with the same material as the bottom is composed of, and the process resumed. A test may be thus tapped about once every 24 hours. The drill is shown in fig. 32.

The concentrated lead is refined on another fresh test, on which the old refiner of the Llanelly Works insisted that not more than 2½ tons should be worked off. Towards the completion of the process the fire should be strongly urged, and the silver on no account be allowed to solidify until every trace of lead has been removed by oxidation. The litharge also, which is produced from this highly enriched lead, should be kept apart on account of its containing more silver than the litharge produced on the first test. If on lowering the temperature at the latter stage of the process, when the silver is nearly fine, *i.e.* when all the lead has been removed, the channel being gradually deepened for that purpose, impurities should be observed to rise to the surface, they must be carefully skimmed off, the heat kept well up, and the process continued until on lowering the temperature again, the surface remains free from impurities. From 2 to 6 hours elapse, during which the silver gradually becomes fine. On the large scale, the phenomenon of sudden brightening at the separation of the last traces of lead does not occur, as in cupellation in an assayer's muffle, notwithstanding the glowing statements to the contrary in chemical books.[3] After the surface has become more or less solid or set, it is suddenly thrown up at various points, with the formation of little volcano-like craters, some even several inches in height, through which oxygen escapes, with violence, and liquid metal it may be is spirted out. This spirting may be a cause of loss, and the surface is pricked from time to time to allow the gas to escape quietly. When sufficiently cold the test with its cake of silver weighing from 5000 to 7000 ozs. is taken out, the cake detached, cleaned from adherent impurities, and then sold; or it may be cut up, re-melted, and cast into open-topped iron ingot-moulds, previously slightly smeared over with oil and dusted with charcoal-powder.

About 10 cwts. of coal at Llanelly were required to refine 1 ton of lead.

According to Mr. Pattinson, 4 fodders of lead (1 fodder = 21 cwts. = 2352 lbs.) may be converted into litharge in from 16 to 18 hours on a test 4′ long, 2′ 6″ broad, and 4″ deep, outside measure, and containing about 1½ cwt. of bone-ash; and 24 fodders of lead can be very easily oxidized in one furnace by three men in a week, with a consumption of about 3 cwts. of coal per fodder of lead.[4]

Dick informs me, that "on a test, like that represented in the annexed woodcuts, from 20 to 25 tons of lead may be refined per week, though in some places not more than 12 tons are refined

[3] Vide Rivot's Principes Généraux; Métallurgie du Plomb et de l'Argent, 2, p. 601:—"L'éclair n'est bien net que dans les coupellations terminées au bois; il passe souvent inaperçu quand on chauffe avec de la houille jusqu'à la fin de l'opération."

[4] Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne. 2. part 1, p. 174 1832.

per week on such a test. The quantity refined in a given time is determined by the blast rather than by the size of the test, the part in which the blast really oxidizes being small. The advantage of a large test is that a large cake of silver may be made. The advantage of a wide breast is that 5 or 6 channels may be cut as one after another wears out. The advantage, however, of a breast so broad as that above shown is not evident, for the writer has always found an 8-inch one able to wear out the sides and bottom; but, except that the cake of silver will be smaller, it will do no harm, there being ample room for oxidation."

The loss of lead in cupelling—or, as it is usually termed, refining—by the English method may be usually estimated at about 5%.

In process of working, the tests become partly saturated with litharge by absorption. They are broken up and the saturated portion is smelted in a slag-hearth or otherwise. Fluor-spar, it will be remembered, is an excellent flux for bone-earth, and is often used in smelting mixtures containing test-bottoms.

German Cupellation (Abtreiben).

The principle of this process is exactly the same as that of the English process, the lead being converted into litharge, and the silver left as a cake. The furnaces, however, employed in the two processes differ notably from each other. In the German furnace the bed is fixed and the roof moveable, whereas the reverse is the case in the English furnace. The material of which the bed is formed should be such as will neither combine with nor reduce oxide of lead. For centuries this material consisted of lixiviated wood-ashes, mixed with a little slaked lime as a binding substance; but what is termed "lime-marl" (Kalkmergel) is much more suitable, and is now generally used. It was not until 1815 that this marl was first introduced at Freiberg, and then many difficulties had to be encountered,[1] though it had been used many years previously with success in some other localities. Marl is stated to have been first applied by Tutschnack at the silver extraction works at Tajova, in the district of Schemnitz, so long ago as 1796.[2]

Formerly wood, being abundant, was used as fuel, and there was not even a roof to the furnace, so that great waste of heat must have occurred. With a view to lessen this waste a roof was added, and it was essential that it should be moveable, in order to enable the workmen conveniently to get out the cake of silver and properly prepare the furnace-bottom, which requires renewal at the end of every cupellation. Moreover, by removing the roof, the furnace can be quickly

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[1] Beschreibung der Freiberger Schmelzhüttenprozesse, 1837, p. 112. I shall avail myself chiefly of Winkler's book in my description of the process, translating literally when necessary.

[2] Karsten's Archiv. 2. ser. 1832. 5. p. 422. There is a paper by Kersten on the introduction of the lime-marl bottoms at Freiberg which contains some interesting matter.

cooled so as to allow of the extraction of the silver without delay, and, consequently, the intervals of time between successive cupellations may be shortened. The furnace to be described is designed for wood as the fuel; but it may be easily modified so as to be adapted for coal, as will be stated in the sequel.

I have selected for special description the process as conducted at Freiberg, with wood as the fuel, and shall add such notices as may be necessary of the modifications of this process as are adopted in other localities.

German Cupellation at Freiberg.

Description of the furnace.—The annexed woodcuts have been copied from well-known lithographs published by authority.

DESCRIPTION OF WOODCUTS (Figs. 33 to 41).

a. Chief drainage channel.

b. Foundation walls.

c. Iron cramps.

d. Small drains.

e. Great ring-wall; formerly it was usually of sandstone set in clay, but is now made of fire-brick.

f. Slag-bottom. The slag is from the lead-smelting furnaces.

g. Brick-bottom. It is set dry, *i.e.* without mortar, but is grouted with thin marl in order to stop up the joints, and so prevent, as far as may be, the percolation of metal. This bottom is covered with a layer of lime-marl from 6″ to 7″ thick up to the top of the great ring-wall *e*, forming the uppermost and true working bottom of the furnace. It is renewed at every cupellation.

h. Iron cramp-ring.

i. Iron hoop.

k. Small ring-wall.

l. Furnace-breast, over which flow the molten lead products.

m. Breast-plate of iron, covered with lime-marl mixture beaten down, so as to form a flat sloping channel for the outflow of litharge.

n. Litharge-channel, provided with an iron door which lets down from above, so as to keep in heat, and, as far as may be, protect the workmen from unnecessary exposure to heat.

o. Charging-hole, through which the lead is introduced and from which the gaseous products of combustion escape. By more or less closing it with a sheet-iron door, the draught through the furnace may be regulated. At the bottom it is covered with an iron-plate.

p. Fire-bridge.

q. Opening above the fire-bridge, through which the flame passes from the fire-place.

r. Twyers. According to Winkler the inner opening or mouth of each twyer is provided with a hanging sheet-iron valve which is raised by the blast, so deflecting the latter upon the surface of the molten lead underneath over a considerable surface.

s. Back or twyer-wall, against which one side of the furnace is built.

t. Air-furnace. The Germans divide the furnace into two parts, one of which they designate cupellation-furnace and the other air-furnace (Windofen).

u. Ash-pit.

v. Ash-hole.

w. Grate.

x. Fire-place. There is no chimney.

Provision must in every case be made for conveying away the lead-fume produced, with a view to condense as much of it as possible, and to protect the workmen from its deleterious action.

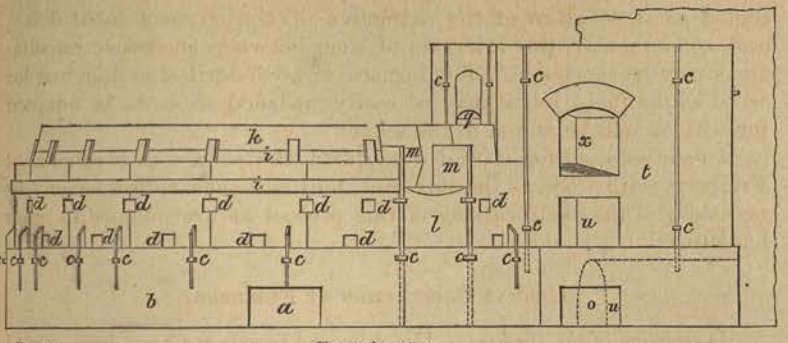

Fig. 33. Front elevation.

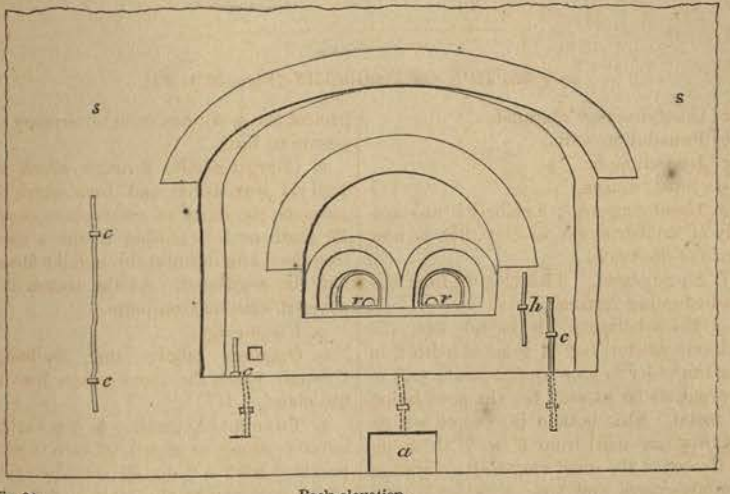

Fig. 34. Back elevation.

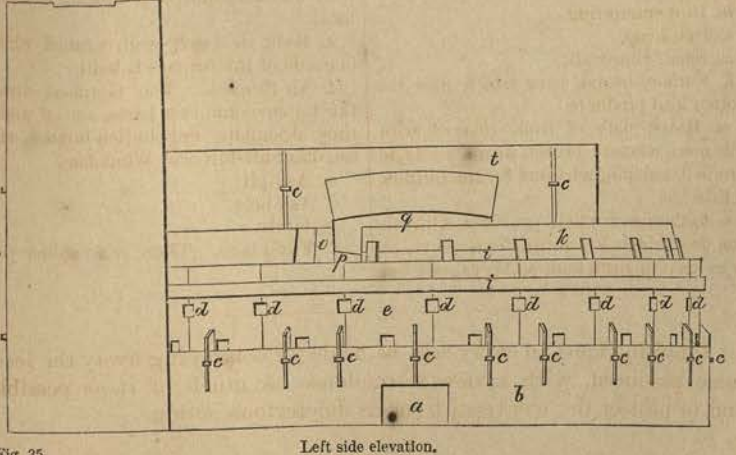

Fig. 35. Left side elevation.

Preparation of the working bottom.[3]—The marl used consists essentially of an intimate mixture of carbonate of lime and clay; and if a natural supply of such a mixture is not at hand, it may be prepared artificially. According to Kersten, the best kind of marl for a cupellation-furnace bottom is composed of 82% of carbonate of lime and 16% of clay, together with a little oxide of iron; and, as a rule, its goodness of quality is indicated by a dark-blueish colour and strong fatty lustre.

At the Altenau Smelting Works, in the Harz, a mixture is made of a natural marl and clay-slate, of which the composition, as well as that of the mixture, is given in the following table:[4]—

COMPOSITION OF MARL, CLAY-SLATE, AND MIXTURE.

	I.		II.		III.
Silica	14.34	.....	59·77	.....	22·24
Alumina	3·44	.....	14·77	.....	5·39
Sesquioxide of iron	3·69	.....	10·61	.....	4·88
Lime Carbonic acid	77·05	.....	1·58 ..	.....	65·65
Magnesia Carbonic acid	2·12	.....	0·51 ..	.....	1·84
Loss by heat	..	.....	4·80	.....	..
Manganese, alkalies, carbon, and loss	..	.....	7·96	.....	..
	100·64	.....	100·00	.....	100·00

I. Natural marl. It often contains *Terebratula biplicata*, and *T. semiglobosa* fossils, which occur in the *chalk-marl* as well as in the contiguous *upper green-sand* formation. II. Clay-slate. III. Mixture.

The mixture consists of 30 cubic feet (Hanoverian; 1 c. f. = about 0·9377 English) and $6\frac{1}{4}$ cubic feet of clay-slate, both in the state of powder.

The following analyses of suitable marls may be instructive.

COMPOSITION OF OTHER KINDS OF MARL.

	I.	II.	III.	IV.
Silica	21·22	21·39	23·06	22·24
Alumina	6·41	5·30	9·17	6·76
Sesquioxide of iron	4·04	3·72	3·21	3·54
Carbonate of lime	66·14	68·28	62·35	66·41
Carbonate of magnesia	2·22	0·81	1·44	1·05
	100·03	99·50	99·23	100·00

I. It is celebrated as marl suitable for German cupellation-furnaces: on exposure to the atmosphere it disintegrates and falls into small sharp-angled parallelopipedons, acquiring a dark super-

[3] See a paper by Kerl and Wimmer, entitled "Ueber das geognostische Vorkommen und die Zusammensetzung der auf den Harzer Silberhütten angewandten Treibmergel. Berg- u. hüttenm. Zeit. 1853, p. 241.

[4] Berg- u. hüttenm. Zeit. loco cit.

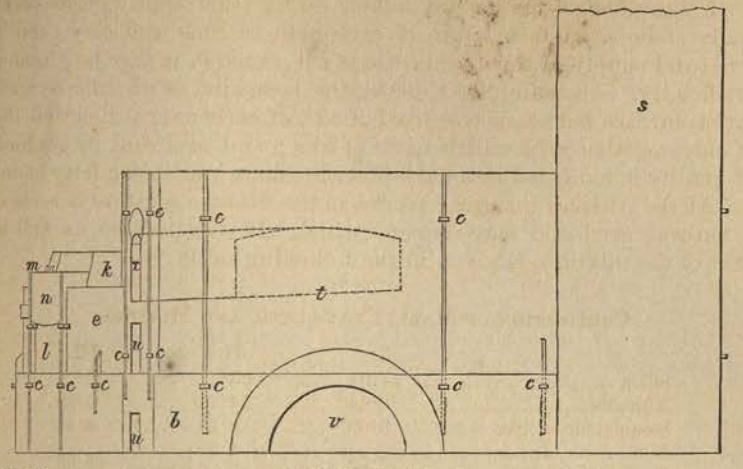

Fig. 36. Right side elevation.

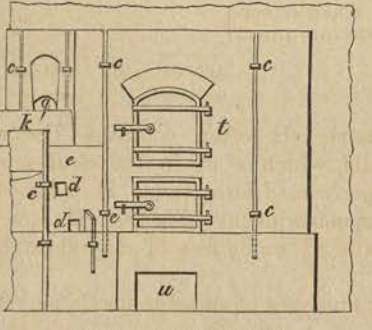

Fig. 37. Front elevation of fire-place.

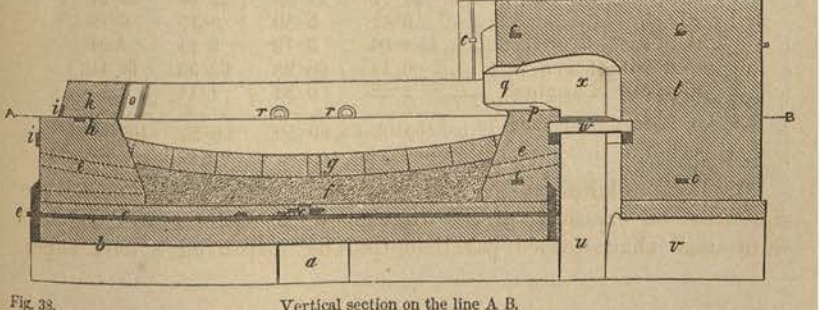

Fig. 38. Vertical section on the line A B.

ficial colouring; it is somewhat unctuous to the touch and adhesive to the tongue; its fracture in large pieces is conchoidal, and in small ones splintery; it contains 28·5% of matter insoluble in hydrochloric acid; it is used without admixture at the Frankenscharn Smelting Works at Clausthal. II. and III. are used in admixture in the proportion of 3 measures to 2. IV. Represents the composition of the mixture of II. and III.; it is employed at the Lautenthal Smelting Works, which are also in the Harz.[5]

From the foregoing analytical data, it appears that good material for the working bottom of a German cupellation-furnace should have a pretty constant composition. Too much clay is injurious, as tending to cause cracks in the bottom, greatly to retard desiccation, and render the bottom too little absorbent.[6] The bottom should absorb as much litharge as will eventually prevent the fine silver from infiltrating. A mixture of dolomite and clay is used at Tarnowitz, in Upper Silesia, concerning which particulars will be given in the subsequent description of the process of cupellation there practised with coal as the fuel.

Winkler states that the marl often contains scattered particles of iron-pyrites, which should be carefully separated, as should also any bits of straw and wood, especially if directed downwards, for the lead follows their track, gets underneath, and heaves up the bottom. The marl is stamped or ground, and sifted to the degree of fineness of moderately fine casting sand, moistened with water, left at rest for several hours, and then thoroughly kneaded: it should just cohere into a lump when squeezed in the hand. As only about half of the marl in a bottom becomes soaked with lead, the other half may be used again, just as in an English test. The brick bottom having been first sprinkled with water, the prepared marl is spread over it to the thickness of about 8″ in the centre and 9″ at the circumference. The marl covering is beaten down solidly, at first with the hand, and afterwards by a suitable instrument, until it is about 6″ thick in the centre and 7″ at the circumference, and so as to follow the curvature of the brick bottom immediately underneath: it is possible to make it either too solid or too loose. Experienced workmen know when it is right by the touch and by the sound produced on beating it down. A blow with the fist should strongly indent it (?), but not the pressure of the hand and thumb. The Germans have the following proverb[7]:—the more concave the bed the easier is lithargification and the more difficult brightening; on the other hand, the flatter the bed the more difficult is lithargification and the easier brightening. In flat beds the lead can more readily escape along with the litharge, which may consequently be richer in silver.[8] When the marl bottom is finished, a shallow circular

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[5] Berg- u. hüttenm. Zeit. loco cit.

[6] Winkler, p. 122.

[7] Je muldiger der Herd ist, um so leichter es glättet und um so schwerer es blickt, dagegen je flacher der Herd ist, um so schwerer es glättet und um so leichter es blickt.

[8] Winkler, op. cit. p. 124.

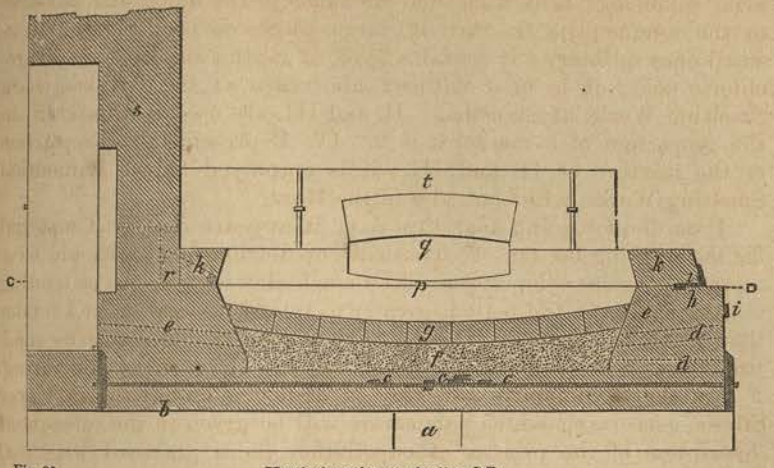

Fig. 39. Vertical section on the line C D.

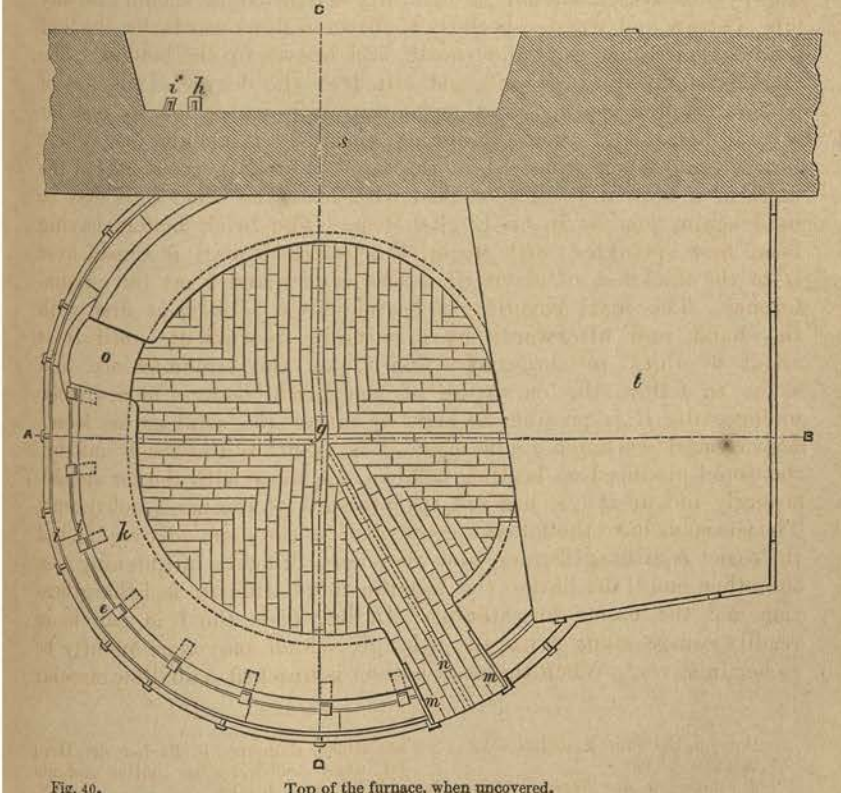

Fig. 40. Top of the furnace, when uncovered.

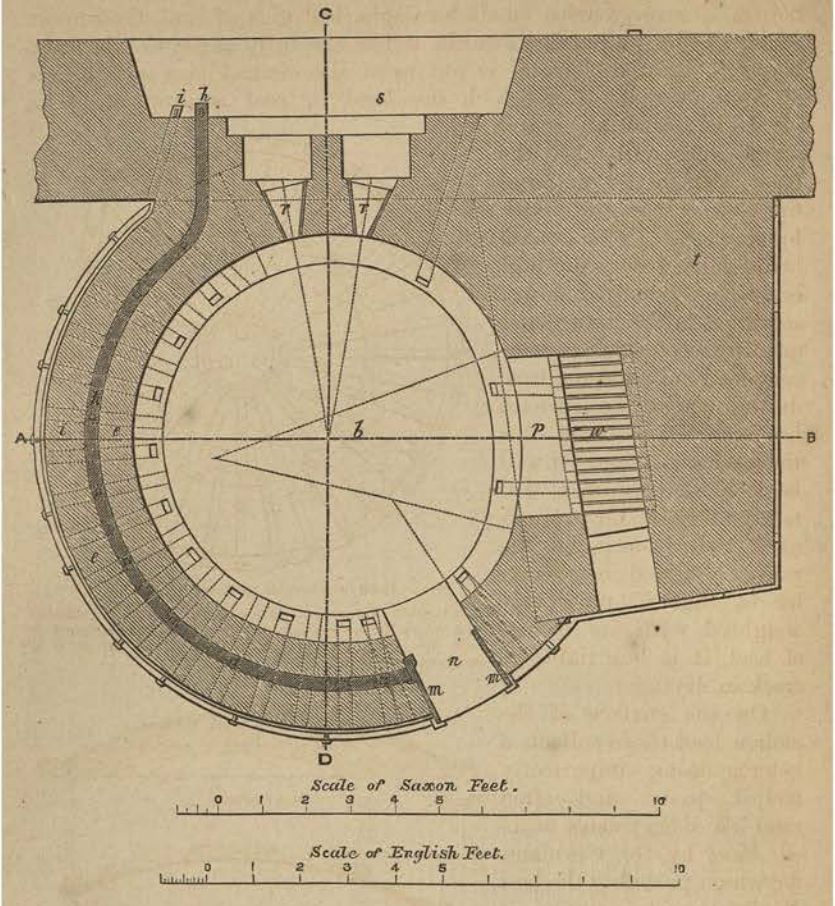

Fig. 41. Horizontal section on a level with the bottom of the twyers.

cavity $\frac{1}{4}$″ deep and from 24″ to 30″ wide is cut out from about the middle of it, but a little nearer the twyers and the fire-place, and in this it is intended all the silver left by cupellation should be collected. The surface of the cavity is beaten solidly down by a large flat-faced hammer.

Mode of conducting the process.[9]—As soon as the marl-bottom has been prepared in the manner described, it is ready for immediate use. Formerly about 100 ctrs.[1] of lead were usually cupelled at Freiberg in one operation, of which from 65 to 80 were introduced at first, and the remainder afterwards at successive intervals. The

[9] I shall follow Winkler's description as closely as I think desirable.

[1] The weight of the centner has been changed since 1859. At the date of Winkler's book, in 1837, from which this account is mainly derived, 1 ctr. (miner's weight) = 114 lbs. 1 lb. = 7193 grains English. 1 lb. Saxon = 1·0275 lb. English. 100 ctrs. = somewhat more than 5 tons.

bottom is covered with small hemispherical pigs of lead, the convex surfaces being placed downwards, and so carefully as not to injure the bottom.[2] Ignited charcoal is put upon the central pigs with billets of wood over it, after which the hood or roof is dropped in its place and luted all round at its edges with clay, the blast is then let on, and fire made on the grate with billet wood. From 3 to 5 hours elapse before the lead is completely melted down, according to the nature and quantity of foreign matter contained in it, and the time during which the furnace has been left to cool after the last cupellation. It will be noted that the marl bottom undergoes no preliminary desiccation; and the reason assigned by Winkler is, that if previously weighted with its charge of lead, it is less liable to crack in drying.

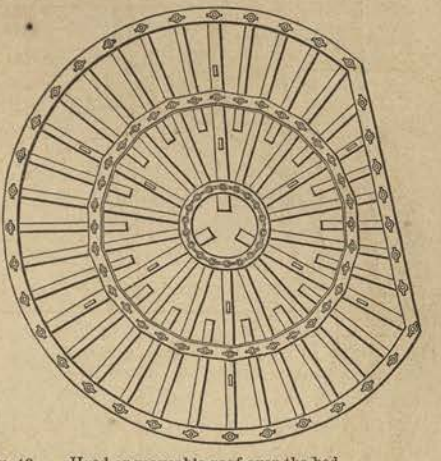

Fig. 42. Hood or moveable roof over the bed.

It is made of iron bars, and on the inner surface is studded with projecting hook-shaped pieces of flat iron, designed to hold the marl-mortar mixed with tow with which it is plastered over.

Fig. 43. Side elevation.

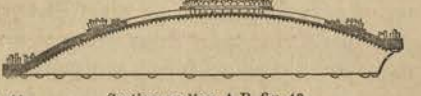

Fig. 44. Section on line A B, fig. 40.

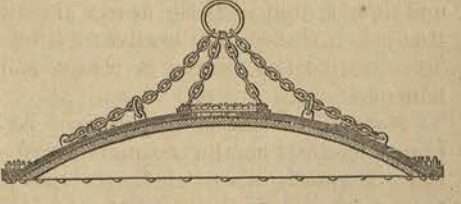

Fig. 45. Section on line C D, fig. 40.

On the surface of the molten lead there collects a heterogeneous, imperfectly melted, pasty, and often sand-like slaggy mass, termed *Abzug* by the Germans, for which probably the best English word is scum: it consists of a mixture of oxide of lead, sulphuretted and arseniuretted metallic substances, and of the marl bottom. The characters, however, vary much, according to the quality of the lead under treatment. The temperature is raised—but not too quickly lest the bottom should be heaved up from the escape of vapour—in order to render the *Abzug* as liquid as possible, and so facilitate its removal by skimming. It is drawn off

[2] It is an old practice to cover the bottom with straw before charging, in order to lessen the risk of its being damaged during the process.

through the litharge-channel, and any metallic lead intermixed with it will rapidly liquate, and should be put back to that in the furnace.

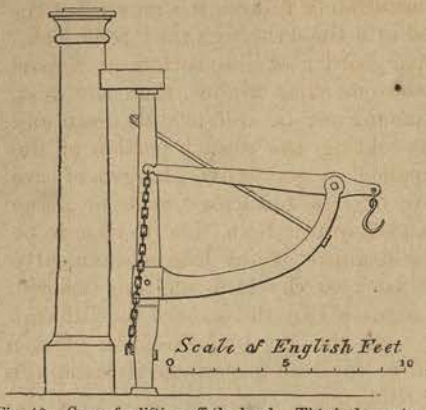

Fig. 46. Crane for lifting off the hood. This is drawn to a smaller scale than the preceding figures.

The skimming lasts about an hour, fresh impurity all the while rising to the surface of the lead; but it scarcely need be added that the duration of this stage will depend mainly on the impurity in the lead. The firing is pushed strongly, and the bath of lead gradually acquires a gentle circular movement. The surface of the bath becomes clear and bright, but is soon again covered with a pasty coating termed *Abstrich*, which is only impure litharge.

At the period of the formation of *Abstrich*, the circumference of the bath of lead gradually contracts, leaving a portion of the bottom all round uncovered, termed "Glättrand" or litharge-border, which evolves bubbles of carbonic acid, and absorbs oxide of lead. The fire is well kept up, and when the permeation of litharge has extended several inches beyond and round the surface of the lead, a furrow or groove is cut with a kind of saw in the bed of the litharge-channel for the outflow of the *Abstrich*. This furrow is at first made as close to the fire-place as possible, because there the temperature is highest, and there, consequently, is the position most favourable to the liquidity of the litharge. After some time it may be necessary to stop up this first groove and make a second, occasionally even a third, just as in the case of cupellation on an English test. The flow of *Abstrich* usually commences about 1½ hour after the removal of the last *Abzug*, and continues about as long, sometimes longer. If, in spite of strong firing, the *Abstrich* should still be too thick to run off, billets of wood are placed upon it and there left to burn away; but usually it is sufficiently liquid wholly to run over the breast down to the ground. As soon as the stream begins to stick to the breast, the operation of withdrawing the *Abstrich* may be considered as ended, and that of the flow of litharge (Glätte) as beginning, when the temperature should be reduced to the proper degree, which can only be learned by experience, and should be maintained at that degree: it must, however, be varied somewhat, according to the nature of the lead under treatment, and Winkler states that it should increase with the proportion of impurities present, especially arsenic, antimony, and iron. Hence it should be raised on the addition of fresh lead of the same kind as that at first put into the furnace, this lead giving rise to the formation of fresh *Abstrich*, which tends to lessen the liquidity of the litharge. Litharge continues to be produced during from 20 to 22 hours, that is, until what the Germans term the "Blick,"

or brightening of the residual silver occurs, which usually takes place 30 or 33 hours after letting on the blast.

The addition of fresh lead immediately follows the removal of the *Abstrich*. Two pigs are introduced at a time, through the "Schürloch," and laid carefully upon the upper border of the bottom, at a part expressly raised for that purpose somewhat higher than the rest, where they gradually melt, and should not be able to slide down and so injure the bottom. After thus adding the second portion of the total quantity of lead to be cupelled in successive charges of two pigs at a time, a stone-like more or less refractory mass or *Abzug* separates, which remains *in situ*, and requires from time to time to be loosened, in order that it may be drained of any lead mechanically diffused in it: this product goes back to the lead-smelting furnace. The supply of fresh lead must be regulated by the state of the litharge channel, care being taken not to raise the level of the bath of rich argentiferous metal on the bottom so high as to promote its escape in sensible quantity along with the litharge.

When litharge first flows, sufficient should be left on the bottom to extend about 15″ beyond the circumference of the bath of lead, forming the litharge-border or "Glättrand;" this border may be reduced to about 10″ and gradually at last to about 5″, as the circumference of the mass of molten metal contracts. Although this covering of litharge may retard cupellation, yet it is advantageous in preventing the escape of lead along with the litharge and lessening the loss of lead and silver by volatilization.

According to Teichmann, when too much litharge is allowed to accumulate on the bath of lead, not only is there greater loss of lead by volatilization, but more litharge is absorbed by the surrounding part of the porous bottom; and more of the latter consequently has to be subjected to the usual treatment for the extraction of the lead from it, which adds to the expenditure as well as to the loss of lead. On the other hand, if the litharge is allowed to flow off too quickly, greater loss of lead occurs through direct volatilization, and the litharge is argentiferous. Part of the silver contained in the lead is oxidized along with the latter, but is again reduced by the subjacent metallic lead if left for a certain time in contact with it: the shorter the period of this contact the less complete is the reduction of the oxide of silver, and the greater the loss of silver, in the litharge.[3]

During the whole of what the Germans term the "litharge-period," bubbles of gas escape from the bottom where it is impregnated with oxide of lead, but they become smaller and less frequent as the work proceeds. Occasionally these bubbles form under the lead itself, and project it upwards in small drops, which fall on and escape with the litharge, thereby causing a loss of silver great in proportion to the degree of enrichment of the lead.

Towards the end of the "litharge-period" the temperature must

[3] Zeitschrift für das Berg-, Hütten- und Salinenwesen im Preuss. Staate, 1867, 15. p. 26.

be considerably increased in order to keep the silver, then nearly deprived of lead, sufficiently liquid and in motion, so as to remove the last portion of lead. The layer of molten litharge becomes reduced to a film, and is then driven off the surface of the silver, towards its circumference. While this goes on fresh particles of litharge rise to the surface of the silver in the form of "dark flowers and clouds, between which the silver, constantly in motion and constantly changing its appearance, shines forth pure and bright," until at last the litharge completely disappears, and the metal becomes motionless. This appearance or brightening is termed "Blick" by the Germans, and the cake of silver "Blicksilber." Immediately afterwards the blast is shut off, and water poured upon the fire as well as upon the silver.

The "Blicksilber" should have a hackly fracture, and contain about 94% of fine silver, the remainder consisting chiefly of lead, with small quantities of copper, nickel, cobalt, and occasionally arsenic.[4] It is not considered desirable to push the refining further in this furnace, which might easily be done by continuing the blast a little longer, because in that case bubbles of gas would escape from the surface of the metal and cause loss by projecting it in fine particles to a distance. Winkler states that the silver may be more easily obtained fine on a marl bottom than on one of wood-ashes. The completion of the refining is effected in another furnace, and the process is termed by the Germans "Feinbrennen," or fine-burning, previously to which the cake is carefully freed from adherent impurities and broken into pieces while still warm.

A specimen of "Blicksilber" in my collection from the Lower Harz, for which I am indebted to Breymann, is a truly beautiful object. It contains numerous large rounded cavities, which have obviously been formed by the escape of gaseous matter immediately underneath the molten metal; and some of these cavities are indicated on the upper surface by corresponding protuberances, showing cracks extending through the substance of the metal. These protuberances are entirely different from the crater-like elevations on the cake of fine silver, caused by the liberation of oxygen from the metal itself in the act of solidification. In the "blick-silver" the cavities are widest at the bottom of the metal and there the edges are rounded. The whole mass of the specimen is composed of an aggregation of distinctly visible crystals, no doubt skeleton octahedrons, such as sal-ammoniac forms in crystallizing from an aqueous solution, or such as may occasionally be seen in lead or pig-iron which has accidentally solidified under favourable conditions, *e. g.*, the formation of a drusy cavity and slow cooling. The parietes of the cells or cavities above mentioned present a fibro-crystalline structure. On the upper surface of the specimen there is a thin layer of vitreous, greenish oxide of lead.

Sometimes, though rarely, the lead finds its way under the marl

[4] Lampadius, Grundriss einer allgem. Hüttenkunde, 1827, p. 240.

bottom and raises it up, in which case it must be immediately tapped off as such an accident is irremediable.

After cupellation the marl bottom is impregnated with oxide of lead, usually to the depth of 2″ in the middle and 3″ toward the side of the fire-place; and the parts so impregnated, after being carefully freed from any metallic particles, are smelted in the ore-furnace. These bottoms, which are termed "Herde," yield from 58% to 65% of metallic lead, and on an average 1½ loth (about ¾ oz.) of silver per centner.

The actual quantity and relative proportions of the accessory products of cupellation must obviously vary according to the nature of the lead treated, but on the average Winkler estimates them as follows from 100 centners of lead:—

	Centners.	Percentage of lead.
Abzug	2	64
Abstrich	5½	73
Furnace-bottoms	21½	60
Impure litharge remaining in the litharge-channel mixed with marl and particles of lead	18	85
Other litharge	66	89
Total	113	

From these data the average loss of lead by cupellation is estimated at about 8%; and when bottoms of ashes were used, it was estimated at about 14%. The loss occurs chiefly through volatilization, and much exceeds what takes place in the English process. If the lead treated be very impure, the loss may not be *chiefly* caused by volatilization.

The consumption of wood is from 220 to 280 cubic feet per 100 centners of lead. Carnot states that heating with coal and gas-generators has been tried at Freiberg, but without success.[5]

In the foregoing description, I have adhered closely to that so long ago published by Winkler, who was as competent to observe the process of cupellation and to record what he saw as any person now living. From his position at Freiberg he had the best opportunities of studying the process, and his published works on the subject as well as that on the Freiberg amalgamation process are still received as authoritative because accurate. I now add all that I find novel with respect to the German cupellation process as practised at Freiberg in the lectures of Plattner, edited by Richter, and published in 1860, a work which of all others should be most correct in what relates to the metallurgical operations there carried on.

At present from 350 to 370 centners (1 ctr. = 50 kilogrammes, not the same as when Winkler wrote: see note, p. 192) of lead are cupelled in one operation, and about 130 are added at the beginning and the rest after litharge has begun to flow off. Only comparatively

[5] Ann. des Mines, 6th. ser. 1864, 6. p. 99.

pure and what is called "refined" lead is treated. On account of the purity of the lead, not more than from 4 to 6 ctrs. of *Abzug* are produced at the most. There is no *Abstrich* or impure litharge, and the quantity of litharge yielded amounts to from 320 to 330 ctrs., of which from $\frac{1}{3}$ to $\frac{1}{6}$ consists of red litharge, which is sold as such, and contains from 0·5 to 0·7 Pfundtheile per ctr. of silver, *i.e.* from 0·005% to 0·007%. The formation of this variety of litharge is promoted by allowing the litharge as it runs from the furnace to accumulate in masses up to the weight of 15 ctrs. and to cool gradually afterwards. The other portion of the litharge containing 0·0001% of silver is revived and the lead Pattinsonized. A single cupellation lasts about 80 hours. From 38 to 40 ctrs. of hearth-bottom, yielding 60% of lead containing 0·00025% of silver, are obtained and go back to the ore-furnace. The wood consumed as fuel is from 162 to 165 cubic feet. The loss of lead amounts on the average to 8%, and is often 10%. The yield of "Blick" silver is from about 520 to 530 lbs., *i.e.* 260 to 265 kilogrammes, which is refined in a small reverberatory furnace.[6] Ore very rich in silver is directly subjected to cupellation by placing it under the pigs of lead in the first charging of the furnace.[7]

Abzug.—Very few analyses of this product have been published, which will not appear surprising, when we consider that it is merely a heterogeneous mixture, necessarily variable in composition according to the nature of the impurities in the lead operated upon. Specimens designated as *Abzug* in my collection from Freiberg and the Lower Harz differ widely in external characters: some are pulverulent and contain numerous bits of charcoal, while others are compact, more or less stone-like, and very heavy.

Composition of Abzug.

	I.		II.
Oxide of lead	35·1		53·1
Oxide of antimony[8]	4·8		0·5
Arsenious acid	..		3·0
Oxide of copper	4·6		1·1
Oxide of iron	5·4		5·4
Oxide of zinc	5·0		4·6
Sulphur	6·8		..
Silica	5·8		
Alumina	0·8	7·2	..
Lime	0·7		
Carbon	..		5·6
Metallic lead	32·4		23·0
	101·4		96·3

I. From Poullaouen, the silica, alumina, and lime were doubtless derived from the marl bottom.[9] II. From Pontgibaud, by Rivot. In

[6] Vorlesungen über allgemeine Hüttenkunde, 1860, 2. p. 256.

[7] Carnot, Ann. des Mines, 6th ser. 1864, 6. p. 100.

[8] Rammelsberg estimates this as antimonious acid (SbO^4).

[9] Berthier, Traité des Essais, 2. p. 742.

the original treatise the total is put as 98·3, which is erroneous. It is a little singular that sulphur does not appear amongst the constituents.[10]

Abstrich.—As previously stated, *Abstrich* is nothing but impure litharge, and as the nature and proportion of the impurity may vary much, the external characters of Abstrich will also vary accordingly. Some specimens in my collection are compact, dense, dark grey, granular-crystalline or somewhat stone-like on fracture, and notably different in appearance from litharge; other specimens are lighter in colour, and more crystalline in structure; and I have received some specimens from German smelting works labelled *Abzug* and *Abstrich* so similar in external characters that they cannot be distinguished from each other.

Composition of Abstrich.[1]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Oxide of lead	63·6	84·4	68·0	82·0	89·5	89·2	95·5	67·6	88·8
Oxide of antimony	28·6	9·0	14·0	17·6	..	5·8	..	..	..
Oxide of arsenic ...	..	..	..	..	0·7		2·3	19·7	6·2
Oxide of copper ...	..	0·8	trace	..	0·2	..	0·5	0·4	..
Oxide of iron	..	..	4·0	..	2·6	0·6	0·3	4·4	..
Oxide of zinc	7·0	5·2	..	..	1·5	..	1·1	0·2	..
Sulphur	..	..	..	0·4	..	..	..	0·3	..
Silica	1·6	..							
Alumina	..	..	14·0	..	..	4·4	..	7·6	5·0
Lime.....	..	..							
	100·8	99·4	100·0	100·0	94·5	100·0	99·7	100·2	100·0

I., II. From Poullaouen, first and last formed respectively: both contained a little sulphur of which the quantity was not determined. III. Second formed from Holzappel: the first formed contained as much as 22% of antimony. IV. Ordinary kind from Villefort: on roasting it loses its black colour and increases in weight, for which the reason assigned is that the greater part of the sulphur contained in it is converted into sulphuric acid, which remains in combination with oxide of lead. V. Pontgibaud, by Fournet: taken at the moment when it became sufficiently liquid to flow over the breast. VI. Also from Pontgibaud, ordinary kind: the formation of Nos. V. and VI. was accompanied with copious evolution of arsenical vapours. VII. From Halsbrücke, Freiberg, by Lampadius. VIII., IX. From Katzenthal, produced from lead extracted from phosphatic and arsenical ores: No. VIII., formed at the beginning, vesicular, greenish-black, and somewhat metallic in lustre; in powder it had a dirty yellow colour, with a greenish tinge: No. IX. was formed immediately before the litharge: it was vesicular, granular in fracture, and greyish-yellow.

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[10] Description des Gîtes Métallifères, antea cit. p. 184.

[1] Nos. I., II., III., IV., VI., VII., VIII., IX., quoted from Berthier, Traité des Essais, 2. p. 742. Berthier, Sur le Traitement métallurgique de la Galène. Ann. des Mines, 3 ser. 1832, 2. p. 121. No. V. Rivot and Zeppenfeld, op. antea cit. p. 184.

In the foregoing analyses Rammelsberg infers that the antimony is present wholly in the state of antimonic acid (SbO^5), and the arsenic wholly in the state of arsenic acid (AsO^5); but this is an inference, especially with respect to antimony, which cannot be accepted without further experimental evidence; and Rammelsberg's own examination of two specimens of *Abstrich* shows the necessity of such evidence.

INCOMPLETE ANALYSIS OF ABSTRICH BY RAMMELSBERG.

Oxide of lead	63·21
Antimonic acid (SbO^5)	18·51
Protoxide of copper (CuO)	0·41
Sesquioxide of iron	2·05
Furnace-bottom	9·00
	93·18

From Clausthal. It was brown and vesicular; its specific gravity was 6·86.

Rammelsberg heated two specimens of *Abstrich* from Siegen in hydrogen, and estimated the loss in weight which occurred as oxygen: they were found to be composed as follows:—

	I.	II.
Lead	53·63	49·31
Antimony	38·25	44·23
Iron	0·15	0·05
Furnace-bottom	1·76	0·24
Oxygen	4·95	5·50
	98·74	99·33

The oxygen, as Rammelsberg correctly remarks, does not nearly suffice to oxidize all the lead and antimony, No. I. requiring 16·85, and No. II. not less than 12·65 of oxygen. These are the results previously alluded to, which at least show the necessity of further proof of the inference that antimony is present in *Abstrich* as antimonic acid.[2]

COMPOSITION OF ABSTRICH, AND OF THE LEAD FROM WHICH IT WAS DERIVED.

Original lead.		Abstrich.	
Antimony	5·816	Silica	2·80
Arsenic	trace	Lime	4·50
Copper	1·570	Magnesia	0·68
Iron	0·021	Arsenic acid	2·15
Silver	0·2651	Antimonic acid	39·45
Gold	0·0029	Protoxide of lead	49·52
Lead (by difference)	92·325	Protoxide of copper (CuO)	0·05
		Sesquioxide of iron	0·53
	100·0000	Silver	0·0508
		Gold	0·0039
		Sulphur	0·06
			99·7947

[2] Lehrbuch der chemisch. Metallurgie, 2nd ed., 1865, p. 375.

These products were from the Imperial Smelting Works at Kapnik; and the analyses were made by M. von Lill and A. Eschka.[3] The proportion of antimonic acid should be particularly noticed.

The foregoing results are interesting and instructive as bearing upon the process of "softening" lead, which consists in exposing the metal, at not less than a red-heat, to the action of the atmosphere. In a chemical point of view the process of forming impure litharge or *Abstrich* is substantially the same as that of scorification, to which reference was made in the introductory remarks on cupellation.

Dark-coloured *Abstrich* has received the name of *black litharge*. The cause of this colour seems mainly to be sulphur existing in the state of sulphide; and it has been previously recorded under the heading of "Silicates of Lead," that these silicates are rendered black and opaque by the addition of sulphur, or of certain sulphides.[4] The subject of the black colouration produced by sulphur in slags, when present in the state of sulphide, has been examined in the two preceding volumes of this work. Berthier, it will be remembered, explained the loss of black colour in the *Abstrich* from Villefort consequent on roasting, by the conversion of sulphur in the state of sulphide into sulphuric acid, and the formation of an equivalent proportion of sulphate of lead, with of course corresponding increase of weight. Now, in a paper by him which was published long before his treatise on assaying, from which the foregoing statement is quoted, he ascribed the black colour of *Abstrich* to the presence of sulphide of antimony, which, he writes, "promptly loses its black colour in roasting, and becomes dull yellow, but *without any sensible change in weight.*"[5] But there must be loss of weight, supposing the sulphide of antimony to be converted into antimonious acid, as will be evident on comparing the weights of sulphur and oxygen in the formulæ SbS^3 and SbO^4.

Litharge.—The external characters of litharge have been previously considered, as well as the conditions which determine the formation of the commercial varieties of this substance. The metallic impurities occurring in litharge in sensible quantity are most frequently antimony and copper; and occasionally zinc, arsenic, and bismuth. Silver, and I believe gold also, may be detected in very minute proportion in all litharge. Bismuth has been found in litharge derived from lead ores of the Upper Harz, though in the ores themselves the metal is in such small proportion that it has not been directly detected. It is stated that in the cupellation of the lead from these ores, the bismuth is not oxidized until shortly before the occurrence of the "Blick;" and that thus becoming concentrated in the last portion of lead removed, it may be detected in the resulting litharge.

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[3] Berg- u. hüttenm. Jahrbuch, 1864, 13. p. 50.

[4] Dick is inclined to attribute the black colour chiefly to copper, as its power to blacken litharge is very great.

[5] Ann. des Mines, 1 ser. 1823, 8. p. 903. Sur l'Abstrich ou Litharge Noire.

COMPOSITION OF BISMUTHIC LITHARGE.

	I.		II.
Protoxide of lead	97·11		58·125
Oxide of antimony (SbO^3)	1·50		..
Sesquioxide of iron	0·19		..
Protoxide of copper (CuO)	0·18		0·281
Oxide of zinc	0·07		..
Oxide of bismuth	0·15		35·250
Oxide of silver	..		0·704
Silica	0·80		3·750
	100·00		98:110

I. From Lautenthal. By Franke.[6] II. From the Oker Smelting Works, Goslar. By Ulrich.[7] The alleged concentration of bismuth, in lead during the process of cupellation cannot be easily reconciled with the statement of Berthier, that bismuth, with the aid of heat, partially at least reduces oxide of lead,[8] for such reduction indicates that the affinity of bismuth for oxygen certainly equals, and probably exceeds, that of lead under the conditions prevailing in the cupellation furnace. It is stated that bismuth becomes in a certain degree concentrated in the "blick-silver," from which it is separated in the subsequent process of refining, when it passes along with the last portions of the lead into the bottom or test: it is dissolved out by cold hydrochloric acid diluted with half its weight of water, and precipitated from the solution first by dilution with water as a basic salt, and then what remains in the supernatant liquor is thrown down by lime.[9]

Elimination of antimony, copper, and iron during the process.—The following interesting and instructive observations on this subject were made at the Imperial Smelting Works at Kapnik in 1861 by Sturm and Mrázek.[1] Refining was conducted according to the German method of cupellation.

	Per cent.		
	Antimony.	Copper.	Iron.
Hard lead before refining	0·375	0·931	trace
Abstrich from the furnace	12·00	3·54	0·16
Black litharge from the furnace	7·08	0·56	0·24
Do. do.	4·80	0·20	0·12
Metallic lead after tapping off into the lead-pot	trace	0·130	trace
Pot-litharge before poling (*bohlen*)?	trace	1·42	0·51
Do. from 1st poling	trace	1·02	0·32
Metallic lead after 1st poling	—	0·473	trace
Pot-litharge after 2nd poling	—	0·15	0·42
Metallic lead after 2nd poling (*Verschleissblei*)	—	0·518[2]	0·012

[The substances above designated as litharge are too impure to be regarded as litharge in England.]

[6] Berg- und hüttenm. Zeit. 1859, p. 67.
[7] Ibid. 1854, p. 112.
[8] Tr. des Essais, 2. p. 613.
[9] Carnot, Ann. des Mines, 6th ser. 1864, 6. p. 107.

[1] Berg- und hüttenm. Jahrbuch, 1864, p. 49.
[2] This is the number given, but surely it should be 0·0518.

The antimony was associated with small quantities of arsenic which were not quantitatively determined. From the foregoing results it appears that while by oxidation antimony may be completely separated from lead, copper is only partially separated.

Hearth-bottom (Herd).—Specimens in my collection are richly impregnated with oxide of lead, indeed so much so as to exhibit on fracture a largely foliated structure and yellow litharge-like colour, to the depth of an inch or so from the surface.

Observations on the Process.

If the lead operated upon is impure, it is plain that in order to produce litharge as free from impurity as may be under the circumstances, the largest quantity possible of lead should be introduced into the furnace at the commencement; for the impurities are first oxidized together with a considerable amount of lead, and flow off in the state of impure litharge or *Abstrich*, and not until they are separated is marketable litharge obtained.[3] Every time, therefore, fresh lead of the same kind is added, fresh *Abstrich* must be formed, which, if not kept apart, will contaminate and deteriorate the whole mass of litharge.

On the proportion of Silver carried off by the Litharge during the Process.

It is interesting to inquire whether during the process of cupellation the proportion of silver in the litharge is constant or not. Rivot and Zeppenfeld have investigated this point at Pontgibaud, and published the following tabulated statement of their results, to which they prefix these remarks:—

"We give, in the following table, the results of the essays for silver of the litharges[4] of the successive pots of an entire cupellation; the specimens have been collected by ourselves; we have been careful to take in the bath in fusion samples of the contained alloy, corresponding to the specimens of litharges. These samples represent almost exactly, as to richness in silver, the shots of lead contained in the litharges. We will call to mind that the first pot of litharge was taken 10 hours after the fusion of the lead, and the last 36 hours after that fusion. It requires about half an hour to fill a pot of litharge, and when the latter is removed there still remain in the furnace about 250 kilogrammes of lead."[5]

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[3] What in this country is known as "German litharge" is cheap, and considered as bad at the price.

[4] I make the plural of litharge for the sake of exactly rendering the French expression.

[5] Gîtes Métallifères, antea cit. 1851, p. 182.

TABLE SHOWING THE CONTENT OF SILVER IN THE LEAD AND LITHARGES DURING AN ENTIRE CUPELLATION.

Numbers of the pots of Litharge.	Grammes of Silver in 100 kilogrammes.		Numbers of the pots of Litharge.	Grammes of Silver in 100 kilogrammes.	
	Lead.	Litharge.		Lead.	Litharge.
1	600	6	24	1268	7
2	588	5	25	1298	8
3	705	7	26	1335	5
4	656	4	27	1439	4
5	686	3	28	1511	4
6	702	5	29	1556	5
7	713	6	30	1637	5
8	740	5	31	1762	5
9	755	4	32	1809	6
10	765	7	33	1959	7
11	779	8	34	2131	6
12	819	5	35	2225	6
13	848	4	36	2388	5
14	849	6	37	2662	4
15	928	7	38	3571	5
16	879	5	39	3631	7
17	969	6	40	3559	5
18	989	4	41	4058	5
19	1008	5	42	4967	7
20	1080	5	43	6599	6
21	1109	4	44	8921	5
22	1143	6	45	11920	6
23	1179	5	...	...	...

The number of Troy ounces of silver in 100 kilogrammes may be found by multiplying the amount in grammes by 0·03208, say 0·0321, and in the ton approximately by multiplying by 0·321, the gramme being taken as equal to 15·4 Troy grains.

The proportion of silver in the litharge depends in a certain degree upon the temperature and rate of refining, being highest during quick and hot work.

GERMAN CUPELLATION WITH COAL AS THE FUEL.

The furnace selected for illustration is that in operation at the Government Smelting Works, designated "Friedrichshütte," at Tarnowitz, in Upper Silesia, which is represented in the annexed woodcuts, figs. 47, 48, 49, 50, copied from the engravings accompanying the recently published description of those works by Teichmann, the director. The following information on the subject is also derived from the same source.[1] The construction of the furnace is essentially the same as that of which an account has been previously given, and will be sufficiently understood from an inspection of the woodcuts without any detailed explanation. The interior of the fire-place, the

[1] Zeitschrift für das Berg-, Hütten- und Salinenwesen im Preuss. Staate, 1867, 15. p. 40 *et seq.*

fire-bridge and the flue are of fire-brick, while the rest of the brick-work is of common brick. The bricks used in the upper ring-wall above the iron armatures are 1′ long, wedge-shaped, and bevilled off inwards. This ring-wall has usually to be wholly renewed once a year, for which are needed from 900 to 1000 bricks, costing 8 thalers (about 24 shillings) per 1000. The lower part of the furnace on the contrary is not exposed to injury. Current repairs are consequently limited to the fire-place, fire-bridge, and flue, and cause proportionately very small expense. There is only one twyer with a semicircular opening or eye. When coal is used the hood or moveable cover must be higher than when other fuel less rich in gas is used. The flue may by means of a damper be put either in communication with the chimney contiguous to it, or with an underground tunnel leading to a series of condensation-chambers connected with a high stack. In the first stage during the melting down of the charge of lead when no lead-fume is evolved, the passage to the former is open

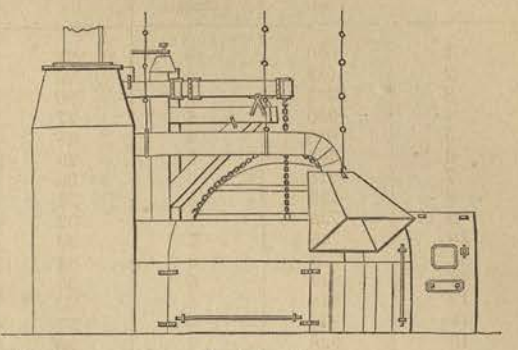

Fig. 47. Front elevation.

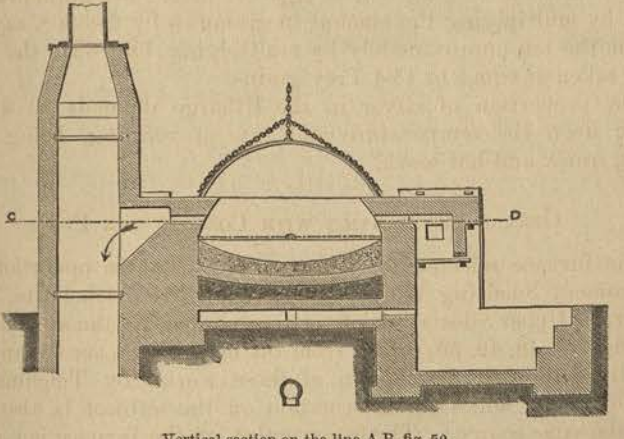

Fig. 48. Vertical section on the line A B, fig. 50.

and that to the latter closed; but when cupellation begins the reverse is the case. The fume which escapes from the litharge-channel is carried into the condensation-chambers through a sheet-iron pipe, as shown in the woodcut, fig. 49.

The hearth-bottom consists of dolomite, from the Upper Silesian

Muschelkalk formation, mixed with from 16% to 20% of fire-clay, and is made in the manner previously described. Two kinds of dolomite in use were found to have the following composition :—

COMPOSITION OF DOLOMITE.

	I.	II.
Carbonate of lime (CaO,CO^2)	50·85	49·60
Carbonate of magnesia (MgO,CO^2)	38·06	37·20
Hydrated sesquioxide of iron ($Fe^2O^3,3HO$)	3·25	2·53
Alumina	1·59	2·00
Silica	5·67	7·85
	99·42	99·18

No. I. has been found very good and better than No. II. on account of its containing less silica.

The hearth-bottom is made deeper or shallower according as it is intended for what is termed poor or rich cupellation, and its capacity varies from 23 to 19 cubic feet for respective charges of 165 ctrs. of poor and about 130 of rich lead. In poor cupellation the object is the production of enriched lead containing about 10% of silver; and in rich cupellation the object is the production of "Blicksilber." At these smelting works the whole charge in both cases is added at once, and there is no subsequent introduction of lead, "Nachsetzen" or after-charge; and the reason assigned is that the latter practice necessitates longer exposure of enriched lead to a high temperature with, consequently, an increased loss of silver; and with respect to poor cupel-

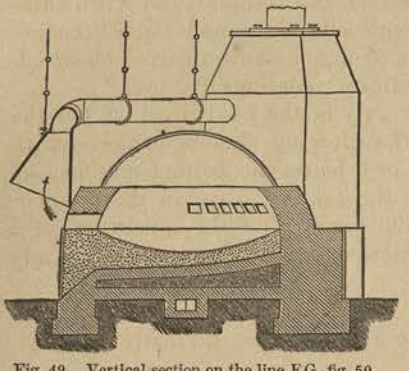

Fig. 49. Vertical section on the line F G, fig. 50.

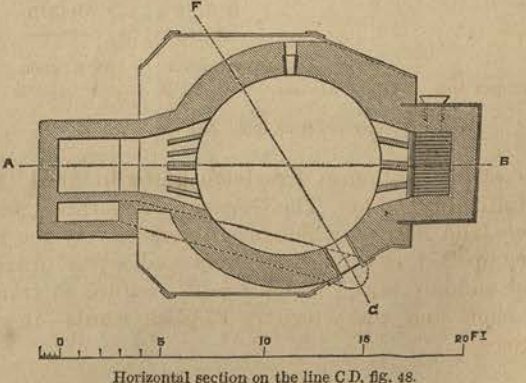

Fig. 50. Horizontal section on the line C D, fig. 48.

lation there is the additional reason that as the litharge produced from it is intended for sale it must be kept as pure as possible. The blast-pipe at the mouth is from $1\frac{3}{4}''$ to $2''$ wide; and under a pressure of $\frac{1}{2}$ lb. per square inch from about 200 to 260 cubit feet of air are delivered per minute. The ingots of lead are cast dish-shaped, having the same curvature underneath as that of the furnace-bottom, in order that in charging they may be the least likely to injure the bottom. The lead is placed crosswise, part in front of the fire-bridge and the rest in front of the flue, so that nearly in a line from the twyer to the litharge-channel the bottom is left free to the width of about $2\frac{1}{2}'$, and, it is stated, it may by this means be more easily dried. It is enjoined that the temperature should be carefully raised and the bottom be dried as much as possible before the melting down of the lead begins and ends, which takes place in 4 or 5 hours. From 100 to 120 cubic feet of blast should be introduced per minute. The depth of the gutter cut for the outflow of the litharge should be such that when the blast is stopped the outflow ceases. In poor cupellation, the residual lead when sufficiently enriched is drawn off through a tap-hole under the litharge-channel, and cast into the dish-shaped ingots above referred to, which are marked with the letter C to indicate "concentrated lead."

At the end of the process not only is the hood lifted off, but the fire-bars are also pulled out and the glowing cinders quenched with water, so that in the course of 5 or 6 hours the bottom may be cool enough to admit of the removal of the cake of silver in the presence of the manager. At the longest, 20 hours after the conclusion of a cupellation, the bottom may be renewed and the furnace made ready for another operation.

The litharge produced in poor and rich cupellation of Friedrichshütte has been found to contain the following foreign matters:—

FOREIGN MATTERS IN LITHARGE PER CENT.

	Poor.	Rich.
Oxide of zinc	0·190	0·120
Sesquioxide of iron*	0·320	0·310
Silver	0·0012	0·0015
	0·5112	0·4315

	dwts.	grains.	dwts.	grains.
Silver per ton	7	20·2	9	19·2

* Derived from tools, &c.

The results of cupellation at Friedrichshütte in 1864, 1865, are given in the following table. The Germans have three good words, *Eingang*, *Ausgang*, and *Abgang*, which mean respectively the weight of lead and silver cupelled, the weight of lead and silver obtained, and the loss of lead and silver, and which I will venture to translate by three equally short and characteristic English words—in-gone, out-gone and off-gone.

RESULTS OF CUPELLATION AT FRIEDRICHSHÜTTE IN THE YEARS 1864, 1865.

Year.	In-gone.		Out-gone.		Off-gone.				For 100 centners of Lead cupelled.					
	Lead.	Silver.	Lead.	Silver.	Lead.		Silver.		Yield.		Consumed.			
	Centners.*	Pounds.	Centners.	Pounds.	Centners.	Per cent.	Pounds.	Per 100 centners of Lead cupelled. Pounds.	Litharge of all kinds. Centners.	Hearth bottoms, Abstrich, and other residua. Centners.	Coal. Centners.	Lime marl. Tonnes.†	Clay. Tonnes.	Wood for lighting fire. Klafters.‡
1864	30070·50	9304·2583	29081·37	9293·2084	989·13	3·29	11·0499	0·0368	88·68	20·80	22·33	2·3	0·4	0·02
1865	24278·14	10201·1291	23673·09	10192·7011	605·05	2·49	8·4280	0·0349	90·75	19·86	23·64	1·92	0·37	0·03

* 1 Centner = 100 lbs. Prussian or Zollverein = 110·232 lbs. English avoirdupois.

† 1 Tonne = 7½ cubic feet Prussian or Zollverein. 100 cubic feet Prussian or Zollverein = 109·184 cubic feet English.

‡ 1 Klafter = 108 cubic feet Prussian or Zollverein.

In 1864 the cost of production of 1 ctr. of litharge packed in a cask of the capacity of 1 ctr. was as under:

	Sgr.	Pf.
Wages	2	5·48
Fuel	1	7·11
Material for furnace-bottom	1	0·37
Contingencies	0	3·93
Blast, maintenance of furnaces	0	7·87
Assorting (*Aushalten*) litharge	0	4·00
Litharge-cask	3	6·60
Closing up (*Zuschlagen*) and repair of litharge-cask	0	5·50
Litharge-cask nails (*Glättfonnennägel*)	0	1·33
	10	6·19

About 1s. English.

REFINING OF "BLICKSILBER."

This operation, which is termed by the Germans *Feinbrennen* (fine-burning), or *Raffiniren* (refining), may be conducted in several ways, all founded on the same principle of separating the residual impurities by oxidation at a temperature somewhat exceeding the melting-point of silver. The ancient method is exceedingly simple and has been well described and illustrated in the treatise of Agricola published more than three centuries ago.[2] It is a method which would not be adopted in the present day except under particular circumstances; but as it is possible that in some parts of the world a knowledge of it might be useful, a rather detailed description of it is here presented. Besides, it is always interesting and instructive to study the metallurgical processes of early times, and the changes which they have undergone. I shall avail myself chiefly of the treatise of Winkler in the following account of this ancient method.[3]

Refining in an open Test with Blast.

"Blicksilber," it will be remembered, contains a sensible proportion of foreign metals, 10% or less; and the problem is the removal of those metals. Now, although it would be practicable to obtain the silver fine, or as the Germans designate it, "Brandsilber," in the first cupellation, yet it would not be economical to do so; because it would in that case be necessary to keep up the temperature of the furnace pretty high for some hours longer; and, as the capacity of the furnace is very large compared with the bulk of silver to be refined, much more fuel would be consumed than were the refining performed in a smaller furnace. Accordingly, a second or after-cupellation is resorted to.

The apparatus required is extremely simple, and consists essentially of what is called the test, which is only a large cupel, and of double

[2] Georgii Agricolæ de Re Metallica. Libri xii. Basileæ. 1561. pp. 385-492. There are five large illustrative woodcuts, showing every detail of the process.

[3] Beschreibung der Freiberger Schmelzhüttenprozesse, 1837, p. 143.

bellows or other machine for producing a constant blast. The test is a bowl-shaped vessel of iron, solidly lined with a substance capable of absorbing molten litharge and of resisting its corrosive action. Formerly that substance was a mixture of $\frac{2}{3}$ of lixiviated wood-ashes and $\frac{1}{3}$ of bone ash properly tempered with water; and for a long time a mixture of sulphate of baryta and bone-ash was used; but in later times the lining was made of the same kind of marl as that of the furnace-bottom itself. The iron bowl is first coated with a mixture of clay and water, and then filled with prepared marl, stamped in so solidly that no impression can be made upon it with the thumb. A hollow is cut out in the marl with a curved knife, from 9″ to 11″ wide and about 3″ deep, leaving a thickness of about $1\frac{1}{2}$″ at the bottom and somewhat less at the rim. The surface of the hollow is brushed over with a mixture of clay and water, then dusted over with bone-ash powder, and finally smoothed with a brass ball. The operation takes place on a flat brick hearth like that of a smith's forge, in which is a cavity to receive the test, so that the rim of the latter may be on a level with the surface of the hearth. The test is bedded in the cavity upon a layer of old marl mixed with ashes. In the twyer-wall, $1\frac{1}{2}$″ above the level of the hearth, is a blast-pipe $\frac{1}{2}$″ in diameter at the mouth. The blast has a pressure equal to 4″ of water, and is directed not towards the centre of the test-hollow, but some inches nearer the blast-pipe.

The charge of "Blicksilber" in pieces, freed from sharp angles, is carefully put into the test, which is only air-dried previously, and piled up as high as possible, so that it may be well permeated by the blast, none being allowed to overhang the edge of the test. Ignited charcoal is placed in front of the blast and the test is surrounded with a sheet-iron hoop, which is filled with charcoal. The blast is let on and the heat urged so that the silver is melted down and is in the usual motion in somewhat less than half an hour. As soon as cupellation has begun the temperature must be moderated, for otherwise great volatilization of silver would occur. The iron hoop is taken away, the charcoal removed from the surface of the silver, as if left there it would retard refining, and thin dry pieces of wood are laid between the twyer-wall and the test, some charcoal being thrown upon the wood in order sufficiently to keep up the temperature. As fast as the wood burns away and embers fall upon the surface of the silver, they must be removed and fresh wood supplied.

From time to time, at least once every quarter of an hour, the silver is stirred up with an iron rod bent round at the end so as not to injure the test, with a view to raise the impurities at the bottom of the bath and expose them to the action of the blast. What are well designated "fat spots" appear on the surface of the silver, which are only molten litharge impregnated with the foreign metals derived from the "Blicksilber," and which gradually during the course of refining find their way to the circumference where they are absorbed by the substance of the test. When these spots have wholly vanished, the end of an iron rod previously warmed is dipped into the silver,

and from the appearance of the pear-shaped drop of silver which remains adherent to it, a judgment is formed whether the silver is sufficiently fine to be cooled: the drop while dull red-hot should be free from spots; in cooling it becomes momentarily spread over with a still deeper, yet equally spotless shade, which is afterwards followed not only by the pure white colour of silver, but especially by the phenomenon of "spitting." As soon as the refining is completed the fire is all removed and the cake of fine silver cautiously sprinkled with hot water until it is solidified. In former times soap and water, and beer were used for this purpose, with the object, it is stated, of improving the appearance of the surface. The cake of silver is removed, and freed from adherent impurities, when it is ready for sale.

It is stated that if the water first added is poured exactly in the centre of the convex liquid mass of silver, spitting seldom or never occurs; on the contrary excrescences readily form in the centre as soon as the water first added strikes only upon the rim, the central portion continuing longer liquid than the rest.

Occasionally it may be necessary to add lead in refining to the extent of from 2 to 4 lbs. to a charge of 50 marks (about 25 lbs. avoirdupois) of "Blicksilber." The time required for refining the usual charge of 50 marks of "Blicksilber" varies according to the quality of the latter from ½ an hour to 3 hours; and the average consumption of fuel at Freiberg in Winkler's day was 2·185 cubic feet of charcoal and 1·240 of wood. The substance of a test contains from 30 to 40, and sometimes from 50 to 60, loths of silver (1 loth = ½ oz.). The dust of the refining house has been found to yield from ½ to 10½ loths of silver per centner.

The opinion of Plattner and Richter on the refining of silver before the blast, compared with refining in a muffle to be presently noticed, is thus expressed: the consumption of fuel is small, and the process is specially adapted for impurer "Blicksilber," which requires powerful oxidation; the management of the process is more difficult and greater attention is necessary; and there is decidedly greater loss of silver through volatilization.[4]

Indian method.—The following account of this primitive method, as it was conducted 300 years ago in India in the reign of the great and wise Emperor Akber, will probably be read with interest.[5] "They dig a hole, and having sprinkled in it a small quantity of the ashes of field cow-dung, they fill it with the ashes of *Babool*-wood (*Acacia Farnesiana*); then they moisten it, and work it up into the shape of a dish or coppel; into this they put the adulterated silver, together with an equal quantity of lead after the following manner: 1st, they put with the silver a fourth part of the lead, and, surrounding the coppel with coals, blow the fire till the metals are melted: this operation they repeat as often

[4] Vorlesungen, 2. p. 263.

[5] Ayeen Akbery; or, The Institutes of the Emperor Akber. Translated from the original Persian by Francis Gladwin. London, 1800, 1. p. 14.

as is necessary; but in most instances four times are required. The proofs of the metal being pure are, the brightness thereof, and its beginning to harden on the sides. When it is hardened in the middle they sprinkle it with water, when, if a flame issues from it, it is arrived at the desired degree of fineness; and if they melt this mass again, there will be lost half a *rutty* in every *tolah*, or six *mashahs* and two *ruttees* in 100 *tolahs*. The coppel becomes a kind of litharge, which, in the Hindostany language, they call *kehrel*, and in Persian, kenneh."[6]

Refining in a Test with Blast under a Muffle.

The heading indicates the difference between this and the last method. It is well illustrated in one of Agricola's quaint woodcuts. According to Kerl this method is in operation at Oker in the Lower Harz, and at the Clausthal Mint in the Upper Harz.

Refining is also effected on a *movealle* bone-ash test in the manner previously explained under the heading English Cupellation, and on a *fixed* test forming the bed of a reverberatory furnace, as will be hereafter described under Ziervogel's process of extracting silver as sulphate in solution from copper or other reguluses.

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[6] For the following note I am indebted to my friend, Mr. Edward Thomas, so well known for his knowledge of Indian coins:—"The official mint *tolah* of Akber's times was exceptionally heavy, ranging up to 186·0 grains. But the scale of proportions may be equally worked out by the ordinary Indian *tolah* of 180 gr., which is divided into 12 *máshas* (of 15 gr.), and the *másha* is equivalent to 8 *ratis* (of 1·875 gr.). Hence the loss (p. 143) per *tolah* of 180 gr. is 0·9375 (or half a *rati*), and on the 100 *tolahs* 93·75 gr. (or 6 *máshas* and 2 *ratis*). See 'Prinsep's Essays' (Murray, 1858), vol. ii.

LEAD-SMELTING.

Historical Notices on Lead-Smelting in Great Britain.

Although no written records exist of the mode in which lead was extracted from its ores in the earliest times, yet it may reasonably be inferred that it was solely by the combined action of heat and atmospheric air, exactly on the same principle as the metal is for the most part obtained at the present day. A lump of galena might attract the eye of a savage by its glitter, but it would be utterly worthless to him for any practical purpose. If, however, he were to throw it on his blazing wood fire, even he could hardly fail to observe the remarkable change it might thereby undergo. The hard brittle ore might in a greater or less degree be transformed, as though by magic, into soft malleable lead; for under those conditions oxide and sulphate of lead would be produced, which, acting upon the unchanged sulphide, would cause reduction of the metal as previously set forth.[1] Poets have suggested that the accidental conflagration of a forest where a vein of galena might have been exposed at the surface, was the means whereby lead was discovered. Speculations of this kind may be amusing, but speculations they will ever remain.

The natives of certain districts in India smelt galena on a small scale, and their simple method is probably nearly the same as, if it be not identical with, that of ancient times, except that they use an artificial blast, whereas there is reason for believing that the smelting fires may in some localities have been urged by the wind alone.

During the Roman occupation of Great Britain lead was produced in various districts, as is proved by the discovery of numerous pigs of lead bearing Latin inscriptions. Many of these are in the British Museum. English archæologists, amongst whom may be specially mentioned Mr. Franks, Mr. Albert Way, Mr. Thomas Wright, and Professor Phillips, of Oxford, have directed their attention to this subject.[2] An interesting point is that some of the Roman pigs present

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[1] Dr. Lamborn, a native of the United States, gives the following notice of lead-smelting:—"The hunter and settler in Missouri, in the United States, early learned to procure the lead necessary for making their shot and bullets by building a fire in the hollow of a fallen tree or in an old stump, and smelting the pieces of galena that they picked up on the surface. The desired metal collected in the ashes, and required only a simple re-smelting to be ready for casting."—A Rudimentary Treatise on the Metallurgy of Silver and Lead, by Dr. Robert H. Lamborn, London, 1861, p. 132.

[2] See Professor Phillips' 'Thoughts on Ancient Metallurgy and Mining among the Brigantes and in some other parts of Britain, suggested by a page of Pliny's Natural History,' and Mr. Albert Way's

the letters EX. ARG., which clearly mean EX ARGENTO, free of silver or desilverized. Mr. Way gives the following list of names on Roman pigs of lead found in England. Britannicus (about A.D. 44–48); Claudius (A.D. 41–54); Nero (A.D. 60–68); Vespasian (A.D. 74–76); Domitian (A.D. 81); Hadrian (A.D. 117–138); Antoninus and Verus (A.D. 163–169).

Mr. Phillips notices the singular fact, that "the inscriptions on these masses of lead, are in the same general form as the marks of the different mines now in work, and which, no doubt, are their literal and lineal descendants. Thus the Ald or Auld Gang mine of Swaledale, old in the days of the Saxons; the mines of Greenhow Hill, in the parish of Ripon, West Riding, which supplied sheet- and pipe-lead for the Roman baths and coffins, at York, as well as tribute to the imperial treasury; the mines of Middleton and Youlgreave (Aldgroove), in Derbyshire, from which the Lutudæ sent not only lead, but 'exargentate' lead from which the silver had been removed —use to this day the pig of the same weight of 1½ cwt., of similar shape, and similar mark to that of eighteen hundred years of antiquity. And, just as at the present day, the countryman whose galloway is tired, drops the leaden load by the way side, for another day's work, so in the days of Rome, the Brigantian lead was thrown down from the tired *caballus* by the side of the ancient mining road on Matlock Moor in Derbyshire, and Dacre Pasture in Yorkshire."

According to Pliny, Britain yielded a large supply of lead, for the following passage occurs in his Natural History: "Nigro plumbo ad fistulas lamnasque utimur, laboriosius in Hispania eruto totasque per Gallias sed in Britannia summo terræ corio adeo large ut lex ultro dicatur, ne plus certo modo fiat."[3] (We use lead for pipes and sheets, more laboriously dug up in Spain and through the whole of Gaul, but in Britain so abundantly in the upper crust of the earth that the law forbade more than a certain quantity should be made.) Archæologists are not agreed as to whether lead was smelted in Britain before the Roman invasion. Professor Phillips has the conviction that it was from the fact that Roman lead has been discovered *not at the mines*, but some miles away from them on a track leading *towards* a Roman or rather a pre-Roman station. That conviction, however, seems hardly as yet to rest on indisputable evidence.

Bishop Watson in his elegantly and lucidly composed Chemical Essays, which I never take up but with increasing pleasure, has treated "Of the Smelting of Lead Ore, as practised in Derbyshire." He says "there are several places in *Derbyshire* called *Boles* by the inhabitants, where lead has been anciently smelted, before the invention of moving bellows by water. These places are discovered by the

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'Enumeration of Blocks or Pigs of Lead and Tin, relics of Roman Metallurgy discovered in Great Britain.' Both papers are in the Journal of the Archæological Society, and in them will be found numerous references to other published notices on the subject.

[3] Sillig's edition, 1851. 5. p. 192. Lib. xxxiv. Cap. xvii. Sect. 49.

slags of lead, which are found near them; there is no certain tradition concerning the manner in which the ore was smelted at these boles, it was, probably, as simple as that of the *Peruvians*, for in *Derbyshire*, as well as in *Peru*, they seem chiefly to have relied upon the strength of the wind for the success of the operation; the boles being always situated upon high grounds, and mostly upon that side of a hill which faces the west. This situation was not fixed upon without design, since the wind blows in England, in the course of a year, near twice as many days from that quarter as from any other."

Watson quotes an author of the 17th century, Joshua Childrey, D.D., to show that lead-smelting in Derbyshire was conducted in this rude way so late as that period. "The lead-stones in the Peak," writes the Doctor, "lye but just within the ground next to the upper crust of the earth. They melt the lead upon the top of the hills that lye open to the west; making their fires to melt it as soon as the west wind begins to blow; which wind by long experience they find holds longest of all others. But for what reason I know not, since I should think lead the easiest of all metals to melt, they make their fires extraordinary great."[4] The language of the first sentence is much like that of Pliny previously cited, namely, "summo terræ corio."[5]

The authority for the foregoing statement concerning the practice of the Peruvians is Alonzo Barba, a Spanish priest and eminent metallurgist of the 17th century. "The natives of Peru," he says, "not yet having bellows to use, employed furnaces in smelting, which they called guairas, and which they still employ. These guairas resemble Castilian furnaces. They only differ from them in being

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[4] Britannia Baconica: or, the Natural Rarities of England, Scotland, and Wales. London, 1661. 12mo. p. 112. I have referred to the original work, and found the quotation correct. It has been well remarked that this volume is "manifestly too small for the performance."

[5] The following list of the sites of ancient Boles was given by Farey in his book entitled, 'General view of the Agriculture and Minerals of Derbyshire,' 1811. 1. p. 382; and it is just possible that accumulations of slag rich in lead may still exist at or in the vicinity of some of these localities:—

Bank, near Holmsfield, ½ m. S.W.
Baslow, N.E. of the Colliery.
Bole-Hill, S. of Sheldon in Bakewell.
" ¼ m. N.W. of Upper Hurst, in Hathersage.
" S.W. of Wingerworth.
" N.W. of Wirksworth.
Chatsworth Old-Park Plantation, S.E. of Baslow.
Cold-harbour, in Lea.
Cromford Moor, S. of the Bridge.
Eyam.
Holy-moor Top, N.E. of Harwood Cupola.
Matlock.
Slag-Hills, S. of Butterly, near Dowayhole Lane, in Ashover.
Stanton in the Peak.
Threebirches, or Pudding-pie Hill, W. of Brampton.
Unthank, ¼ m. W., in Dronfield.

"The sites of these ancient Boles or wind-smelting places are easily found, from the sterility of the spots, and the want of any herbage except a few minute weeds upon the ancient slag and ashes; but here, as well as on the ancient mine-hillocks, the *Campanula rotundifolia* will be found, a diminutive plant, which my worthy patron Sir Joseph Banks has observed to be peculiar to spots where lead abounds in the soil, and which cannot be made to live, perhaps, in any other situation." Now this campanula is very common throughout England, so that Sir Joseph must either have been ignorant of British botany, or lead must be exceedingly prevalent in British soil, where it has not even to this day been detected.

filled on all sides with holes through which the air enters when the wind blows, which is the only time that metal can be smelted. It comes out at the lower part from each of these holes, like little ears, where there is charcoal on the outside, in order that the air may enter hot. These furnaces are placed in high situations, and where there is most air."[6] At the present day furnaces constructed on a similar principle have been recently in operation in the south of Spain for the smelting of certain kinds of poor lead ore, but in which the draught has been produced by a chimney.

Boles, also termed Bayle Hills, are stated to occur in the mining districts of Northumberland, Cumberland, and Durham, as well as in Derbyshire. According to Forster, they were simply piles of stones placed round a fire, on the western brow of an eminence, as near as possible the mouth of the mine, and so arranged as to leave openings which served for the admission of air and the escape of the gaseous products of combustion. Fuel was supplied from the neighbouring woods, which on that account were called *Hag-hill* or *Hag-bank*.[7]

In the course of time an artificial blast was resorted to as a substitute for capricious natural currents of air, and the effective little furnace, termed the Ore-Hearth, was introduced. This furnace is still in operation in the northern lead-yielding districts, and is well fitted for the smelting of rich ores, in localities where coal is dear and peat cheap. My friend, the late Mr. Hugh Lee Pattinson, of world-wide renown as the inventor of the desilverization process which everywhere bears his name, often expressed to me his opinion that for pure rich sulphuretted ores it is superior to the most approved reverberatory furnaces of the present day. Formerly it was the only furnace employed in Derbyshire, but that was about 1730; and when Bishop Watson published his essay on lead-smelting, "there were not above one or two of these *ore-hearths* in the whole county of Derby."[8]

The reverberatory furnace was the last introduced, as might reasonably be anticipated on account of the scarcity and increasing cost of wood as fuel and the abundant supply of comparatively cheap pit-coal. It was known as the Derbyshire Cupola. Schlüter, according to Bishop Watson, states that the reverberatory furnaces in use in Flintshire for smelting lead ore were invented towards the year 1698 by a physician named Wright. On referring to the original work by that celebrated old metallurgist, I find the following passage: "Dieser

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[6] Métallurgie, ou l'Art de Tirer et de Purifier les Métaux; traduite de l'Espagnol d'Alphonse Barba. A la Haye, 1750. Livre quatrième, chap. 6. tome i. p. 272. Arte de los Metales en que se enseña el verdadero beneficio de los de oro, y plata por açogue. El modo de fundir los todos, y como se han de refinar, y apartar unos de otros. Compuesto por el licenciado Albaro Alonso Barba, natural de la ville de Lepe, en la Andaluzia, Cura en la Imperial de Potosi, de la Parroquia de S. Bernardo. Madrid, 1640, p. 79, 80. This is the best edition. See Appendix for an account of lead-smelting in England in the 17th century.

[7] A Treatise on a section of the Strata, from Newcastle-upon-Tyne to the mountain of Cross Fell, in Cumberland; with remarks on Mineral Veins in General. By Westgarth Forster. 2nd ed. 1821, p. 364.

[8] Chemical Essays, 1782. 3. p. 273.

Schmeltz-Ofe worin die Bley-Ertze in Engelland mit Stein-Kohlen geschmoltzen werden, ist in dem Fürstenthum Wallis oder Wales zu Flintshire observiret worden. Es sind auch dergleichen in Engelland zu Bristoll, worin Kupfer-Ertze verarbeitet werden. Solcher ist ein Wind-Ofe und hat kein Gebläse, darin die Feurung mit lauter Stein-Kohlen unterhalten wird, soll ohngefehr Anno 1698 von drey curieusen Leuten inventirt worden seyn, wovon einer, Namens Whrigt, ein Doctor Medicinæ und Chymicus, der andere ein Goldschmidt, und der dritte ein curieuser Mann gewesen, welche daran viel Geld und Zeit gewandt." [9]—(This smelting-furnace in which lead ores in England are smelted with pit-coal, has been observed in the principality of Wales, in Flintshire. There are also the like in England at Bristol, in which copper ores are treated. Such a wind-furnace, without any blast and heated with pit-coal alone, was invented about 1698 by three ingenious persons, of whom one, of the name of Whrigt (a misspelling for Wright), doctor of medicine and chemist, another a goldsmith, and the third an ingenious man, who applied much money and time to it.) Schlüter then goes on to describe the details of construction.

Farey states that "the *Cupolas* or low-arched Reverberatory Furnaces now (1811) exclusively used for the smelting of lead ore in Derbyshire, were introduced from Wales by a company of Quakers, about the year 1747, the first of which was erected at Kelstedge, in Ashover; but this is now disused and pulled down." [10] He published a good account of the most approved cupola-furnace of his day and of the mode of smelting. The furnace was essentially the same as that now in use.

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[9] Gründlicher Unterricht von Hütte-Werken, etc. Von Christoph. Andreas Schlüter. Folio, 1738, p. 110.

[10] Op. cit. 1. p. 385. He gives the following list of localities of cupolas in Derbyshire:—

Barber-fields, in Dronfield (formerly).
*Barbrook, in Baslow (Thomas and John Barker).
*Bonsal Dale (Evans and Co.).
Bradwell (Benjamin Barber).
Bretton, in Eyam (Samuel White).
Calow, E. of Hathersage (the late William Longsdon).
Coppy-nook, in Stanton-Harold, Leicestershire (Earl Ferrers).
Cromford Moor, Steeple House (Charles Hurt).
Devil's Bowling-alley, in Alderwasley (Francis Hurt).
*Ecton, in Warslow, Staffordshire (Duke of Devonshire).
Harwood-Moor near Loads (George Barker and Co.).
Kelstedge, in Ashover (two formerly).
*Lea, near Cromford (Shore and Co.).
Lumsdale, in Matlock (formerly).
Middleton Dale, in Stoney Middleton (George Barker and Co.).
* Stanage, in Ashover (Sykes, Milnes, and Co.).
Ditto ditto (George Barker and Co.).
*Totley (George B. Breaves).
Via-Gellia, in Bonsal Dale (Saxleby and Co.).
Wirksworth, E. of the Town (Charles Hurt).

A Slag-hearth, or, as it was termed, Slag Mill, was attached to the furnaces indicated by an asterisk.

Farey adds, "several of the smelters in the above list are doing but little, and some have their works shut up occasionally, owing to the supply of ore being now so greatly inferior to what it was 20 years ago (*i.e.* about 1790). At Middleton Dale, ore is smelted for the miners and buddlers at 14*s.* for a charge of ore, usually about 18 cwt., and 13*s.* for a charge of belland, or dust-ore, usually about 12 cwt.: and in these cases the miners sell their pieces of lead, instead of their ore, to some of the smelters, who are, I believe, the only lead-dealers in the district."

Bishop Watson thought that Beccher, the German miner and metallurgist, and author of the 'Physica Subterranea,' "might probably have a prior claim to its invention or introduction from Germany." Indeed Beccher asserted that he first applied pit-coal in Cornwall to the smelting of tin ore. Thus in the dedication of his tract, entitled 'Alphabethum Minerale,' written at Truro, to Robert Boyle, he says: "Ignis usus, ope flammarum lithontracum stannum et mineralia fundendi, Cornubiæ hactenus incognitus, *sed a me introductus.*"[1]—(The use of fire, by means of the flame of pit-coal in smelting tin and ores, hitherto unknown in Cornwall, but by me introduced.) Whoever may have first applied the flame of pit-coal to such purposes, there is not, so far as I know, any evidence to favour the notion that the application originated in Germany, where wood continued abundant long after it had become too scarce and costly for metallurgical operations to be profitably conducted in Britain. It was necessity which in this country led to the adoption of pit-coal as a substitute for wood, and the reverberatory furnace was the result. Who Wright, the doctor-chemist, may have been, I know not. No such name is recorded amongst the patentees of the end of the 17th century, though other names occur in connection with the introduction of the reverberatory furnace, especially for lead-melting with pit-coal. In 1678 the patent-right was granted to George Lord Viscount Grandison, "to melt and refine lead oare in close or reverberatory furnaces with pitt coale or sea coale," etc.; and 1690, John Hodges obtained a patent for "a way for melting and refineing lead ore in close or reverberatory furnaces with pitt coal," etc.[2] It is worthy of note that Barba in 1640 described a reverberatory furnace with wood as the fuel for roasting. He uses the very term in Spanish of "hornos de reberberacion,"[3] furnaces of reverberation.

The reverberatory furnaces used for lead-smelting in Great Britain are of two kinds, the Flintshire furnace and the flowing-furnace. In the Flintshire furnace, properly so called, the slag is drawn out in pasty lumps, or in some localities thoroughly melted and then "run out" through the tap-hole, when it is technically termed *drawn-slag* and *run-slag* respectively. The Flintshire furnace is fitted for calcining as well as smelting. It has been asserted that certain impure ores of lead can only be smelted in blast-furnaces; but it is not so. Any ore may be smelted in the reverberatory furnace as well as in the blast-furnace, though less advantageously in some cases.

INTRODUCTORY OBSERVATIONS ON LEAD-SMELTING.

Ores of lead.—The ores of lead are of two kinds, those in which the metal is combined with sulphur, and those in which it is combined with oxygen: the former is represented by galena, which

[1] Watson's Chemical Essays, 1. p. 33, and 3. p. 274.

[2] See Abridgments of the Specifications relating to Metals and Alloys, 1861, pp. 6, 7.

[3] Op. cit. Lib. 4. Cap. 4.

is by far the most abundant, and, therefore, the most important source of lead; and the latter by carbonate, sulphate, phosphate, or arseniophosphate, and molybdate of lead. Hence the mode of extracting the metal must vary according as it is derived from one or other of these classes of ores, which may be conveniently designated sulphuretted and oxidized ores. But in some cases these classes occur naturally in association; and not unfrequently the galena delivered to the smelter is mixed with a little carbonate of lead, the proportion of which however is too small to necessitate any change in the process of smelting. The nature and quantity of the associated vein-stuff must also be considered in determining the most suitable method of smelting to be adopted.

Presence of silver in the ores of lead.—All galena, as well as other ores of lead, contains silver, though not always in sufficient quantity to admit of its profitable extraction. The ores of lead are, consequently, designated as argentiferous or non-argentiferous, according as they contain silver in proportion adequate to pay the cost of its extraction or the reverse. In every case, whatever method of smelting be adopted, the silver in the ore passes into the lead reduced, with the exception of a small quantity which may be retained in the slag, or in the regulus or speise, occasionally accompanying the reduced lead.

Classification of Smelting Processes.

Desulphurization of Galena.—This may be effected as follows:—

I. By what has been designated *method of reactions*, of which the principle is essentially the same, *mutatis mutandis*, as in the usual processes of smelting sulphuretted ores of copper. It is founded on the fact that when sulphide of lead is intimately mixed either with protoxide of lead or sulphate of lead, or with both in such proportion that the oxygen and sulphur in the mixture are in the same proportion as those elements exist in sulphurous acid, and the mixture is heated to a certain degree, complete reduction of the lead takes place, the oxygen and sulphur entering into combination, and escaping as sulphurous acid. The term *method of reactions* is unmeaning as a distinctive appellation, for every lead-smelting process is a method of reactions. The term *air-reduction process* suggests the agent by which desulphurization is effected, just as in another process the word iron indicates the agent by which the lead is separated in that process. The German expression "roast-reactions process" is preferable to that of method of reactions.

II. By roasting and subsequent reduction of the oxidized products wholly or mainly by carbonaceous matter.

III. By the so-called "precipitation process," in which metallic iron is employed as an accessory agent of desulphurization, or an oxidized compound of iron, which during the process will yield metallic iron. I shall designate this process the *iron-reduction process.*

In some cases two or even all three processes are employed in combination.

DEOXIDATION OF OXIDIZED ORES OF LEAD.—In the smelting of such ores, carbon, or iron, or both, are resorted to as agents of reduction.

AIR-REDUCTION PROCESS.

Let us suppose that the substance to be operated upon is pure sulphide of lead, in a comparatively fine state of division, and that the material of the furnace is absolutely proof against corrosion by sulphide, oxide, or sulphate of lead; and let the furnace be reverberatory of suitable construction. Now, the first step is the roasting of the galena, with free access of air, so that it may not clot, and the product may consist of a mixture of protoxide, sulphate, and sulphide of lead, which shall contain oxygen and sulphur in the same ratio as in sulphurous acid. The next step is to raise the temperature sufficiently to cause the reaction between the oxidized compounds of lead so generated and the unchanged sulphide of lead, whereby the whole of the lead may be reduced to the metallic state, while the whole of the sulphur is evolved as sulphurous acid. In this case reduction would be due to the joint action of heat and atmospheric oxygen. But it is hardly necessary to remark, that the precise theoretical conditions here supposed could not be fulfilled in practice, however carefully manipulation might be conducted. The consequence is that, while every effort may be made to approximate to those conditions, there will remain in excess at the conclusion of the process either sulphide of lead or a mixture of protoxide and sulphate; and in practice the latter mixture is always in excess, and a notable quantity of lead is always left unreduced. In order that perfect reduction should occur, it would be necessary not only that the unchanged sulphide and the products of oxidization should be in the exact proportion indicated by theory, but that the mixture of the two should be most intimate, much more intimate indeed than it is conceivable should result from the most active and persevering rabbling. As an unreduced oxidized residue is formed, it becomes necessary to subject that residue to a deoxidizing process in order to extract the lead from it; and, as above stated, carbon or iron, or both, might be adopted for that purpose, reduction being effected either in a reverberatory furnace or in a blast-furnace. Thus, in order to separate the lead in the air-reduction process, two distinct operations are required, one of oxidation, and the other of deoxidation. No account is here taken of that portion of the lead which is volatilized, and which by means of proper condensing arrangements may be in great part recovered.

A reverberatory furnace is not essential to the air-reduction process, which may be conducted in a small blast-furnace so constructed and worked as to cause active oxidation of the sulphide of lead, and in this case oxidation and reduction take place *pari passu*. In such a furnace it is not practicable any more than in the reverberatory furnace to prevent the formation of a residual product rich in oxidized lead.

Hitherto the principles involved in the reduction of lead from its state of combination with sulphur have been considered with respect to the imaginary case of the treatment of pure sulphide of lead in furnaces absolutely proof against the corrosive action of the sulphide and of the products of its oxidation, conditions which can never occur in practice. Pure sulphide of lead is never the subject of metallurgical treatment, and furnaces incapable of corrosion by sulphide of lead or by the products of its oxidation are unknown. Various so-called foreign matters, such as those with which galena is associated in nature, and which have been previously enumerated in this volume, are always found in greater or less proportion in the galeniferous ore delivered by the miner to the lead-smelter. Some of those matters may be so intimately mixed with the galena, and others, though not intimately mixed with it, may have so high a specific gravity, as to render their approximately complete separation impracticable even by the most efficient and most carefully-conducted operations of dressing on the part of the miner. In such cases efforts to carry the purification of the galena beyond a certain point would necessitate the loss of so much galena, that the pecuniary loss arising from that source would far more than counterbalance the inconvenience and attendant increase of expense caused by the presence of those matters in the process of smelting. Moreover, in the case of highly argentiferous galena, considerable loss of silver would inevitably result from efforts pushed too far in that direction. The purer the galena, the more cheaply may it be smelted. But suppose two galeniferous ores to contain when raised from the mines the same proportion of lead, and one to be poor while the other is rich in silver. The elimination of foreign matter from the former might be profitably carried to a much greater extent than from the latter, notwithstanding a notable corresponding loss of lead. With respect to the treatment of all argentiferous galena, properly so called, in a practical sense, the object of the lead-smelter is as much the extraction of silver as of lead; and according to the proportions in which these metals are associated in any particular ore, it is for the miner to determine experimentally how far the dressing of such ore may be profitably carried. Much will depend upon the *nature* of the foreign matter in an ore, whatever may be the process of smelting adopted, as will hereafter be particularly demonstrated. The preceding observations apply with equal force to the iron-reduction process, and mixed air- and iron-reduction processes of smelting galeniferous ores. The influence of particular foreign matters on the smelting of these ores will be considered and exemplified in the description of the various processes in the sequel; for, in my judgment, it is not possible properly to understand and rightly to appreciate that influence without first acquiring a detailed knowledge of the processes themselves.

In the air-reduction process both kinds of furnaces are in use, reverberatory and blast: they will be described in the following order.

Reverberatory Furnaces.

1. *Flintshire furnace.*—The lead is allowed to accumulate in the furnace and is tapped out. The residue is raked out in pasty lumps, and is called grey-slag or drawn-slag, or in certain cases is tapped out in a molten state, when it is called run-slag.
2. *Spanish furnace (Boliche).*—The remarks on the Flintshire furnace apply equally to the Spanish.
3. *Flowing-furnace.*—The ore is calcined in a separate furnace; the reduced lead is allowed to accumulate in the furnace and tapped out. The residue is tapped out in the molten state, and is called run-slag.
4. *Bleiberg furnace.*—The lead runs out of the furnace as quickly as it is reduced. The residue is pasty, and the lead contained in it is extracted from it in the same furnace.

Blast-Furnaces.

5. *Ore-hearth.*—The calcination and reduction of the ore occur *pari passu*, and the residue is raked out in pasty lumps.

SMELTING IN THE FLINTSHIRE FURNACE.

Description of the furnace.—An arched vault, called the air-vault, extends longitudinally under the bed, and at the fire-bridge end it freely communicates with the external air (figs. 51, 52, 53, 54, 56). On the crown of this arch, extending right and left, a level course of brick-

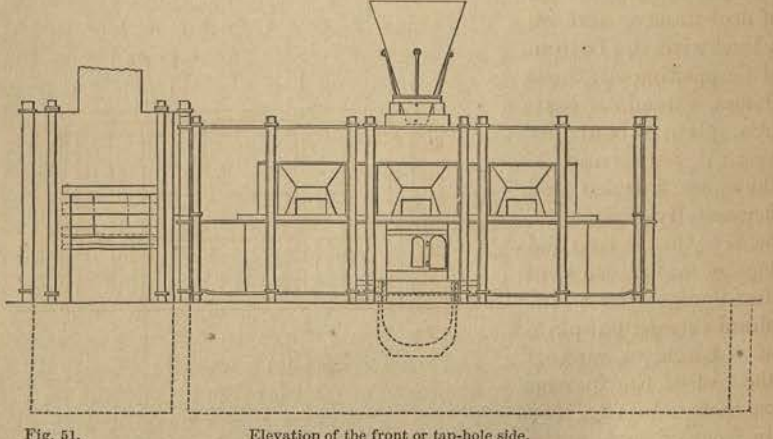

Fig. 51. Elevation of the front or tap-hole side.

work, called the cramp-course, is laid (figs. 54, 56); and on this are placed iron cramps which hold the lower ends of vertical wrought-iron standards (figs. 51, 52, 53, 56, 60). Upon the cramp-course a concave bed of common brickwork, grouted with lime-mortar, is raised solid, sloping from the back as well as from each end to the tap-hole in

front. The edges of the bricks towards the concavity are left sharp, the bricks being set gradually back in each successive course, thus forming, as it were, a series of steps (figs. 54, 56). At the front and back are three openings at equal distances and of the same dimen-

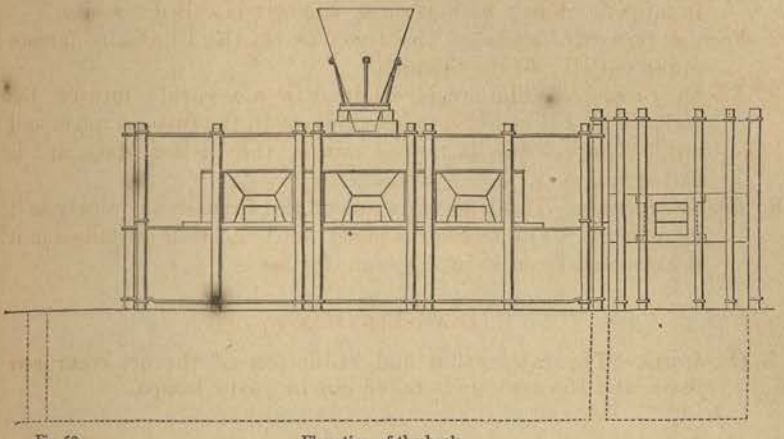

Fig. 52. Elevation of the back.

sions (figs. 51, 52, 54, 56, 57). These openings are formed by strong cast-iron door-frames, of which the tops are bevilled off towards the interior of the furnace, and the bottoms bevilled so that the frames may stand firmly with a slight inclination inwards (figs. 54, 61 *a*, *a'*). In front of both series of door-frames, and on a level with the bottom of the openings in these frames, extends a cast-iron plate about 10′ long, ½″ wide, and 2″ thick, set flatwise and horizontally (figs. 51, 52, 56, 57). On the bevilled tops of each series of door-frames rests inclined a strong flat plate of cast-iron, to support the roof of the furnace on each side (fig. 56). In front of each series of door-frames, plates or jambs of cast-iron about ¾″ thick are placed vertically. There are four castings for each series, those at the ends, right and left, being different from those on each side of the middle door (figs. 61, *b*, *c*, *d*). On the sloping edges of these jambs at the top rests inclined the cast-iron plate above mentioned (figs. 51, 52, 56). Thus each door-frame is

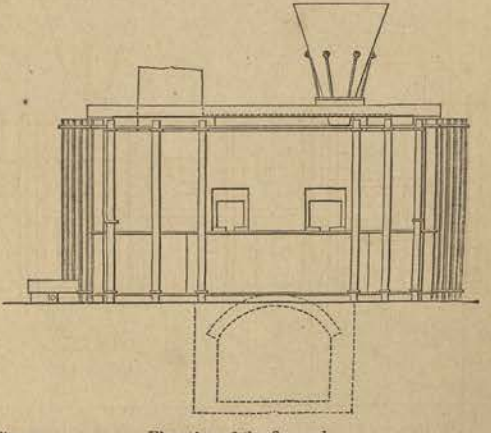

Fig. 53. Elevation of the flue end.

recessed (figs. 56, 57). At the front of the furnace below the middle door-frame is a large plate of cast-iron, called the tap-hole plate, strengthened by a longitudinal projecting rib at the top and bottom. In the middle of the tap-hole plate is a narrow vertical opening, fitted

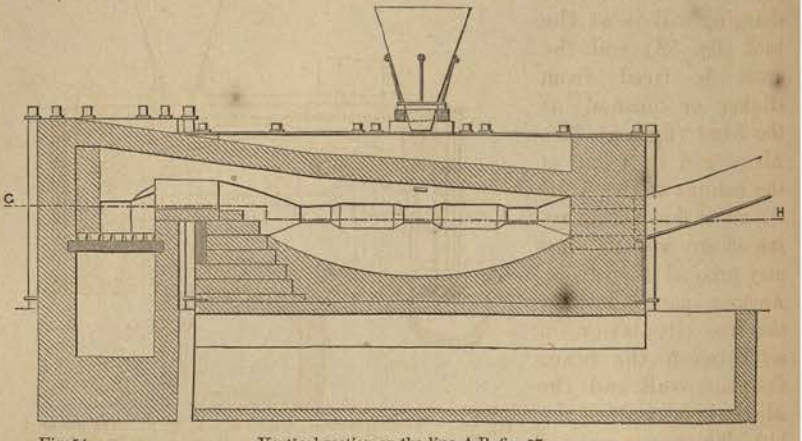

Fig. 54. Vertical section on the line A B, fig. 57.

with a hinged door; and below the bottom of this door is the tap-hole (figs. 51, 56). Immediately under the tap-hole plate and facing the tap-hole is a circular pot of cast-iron, much thicker at the bottom, called the lead-pot, lead-pan, or lead-kettle. In the edge contiguous to the tap-hole is a notch. The bed is covered in above with a low flat arch firmly supported on either side, as above described, and extending from the end wall of the fire-place to the opposite or flue-end of the furnace. Immediately above a line drawn from the middle of the door-frame nearest the fire-place at the front to the middle of the opposite door-frame at the back, the arch presents a very obtuse angle, upon the importance of which stress is laid by the builders of these furnaces. From the middle of this line to the lower surface of the arch vertically above, the distance should be 17″; from the middle of a similar line drawn from the door-frame nearest the flue to the opposite door-frame, the distance to the top of the arch vertically above should be 13″; and from the middle of

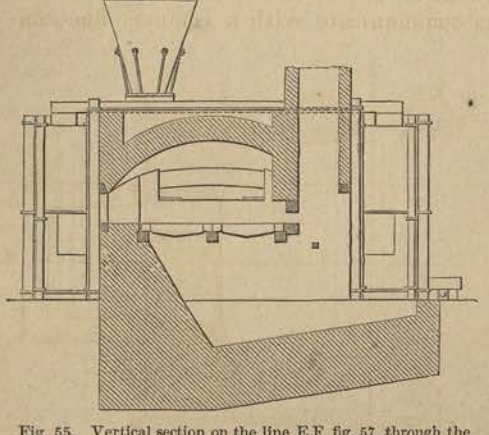

Fig. 55. Vertical section on the line E F, fig. 57, through the fire-place.

the top of the fire-bridge to the top of the arch vertically above it, the distance should be 19″ (figs. 54, 56). In the roof facing the middle door-frames, but nearest that at the front, is an opening, through which the furnace is charged from a bin or hopper above (figs. 54, 56). The fire-hole for charging coal is at the back (fig. 52), and the grate is freed from clinker or cleaned at the front (figs. 51, 55). Above and in front of the ash-pit at the front is a short flue for carrying off any vapour that may proceed therefrom. An open space is left for the free circulation of air between the inner fire-place wall and the adjacent end-wall of the bed. The upper part of the latter wall under the fire-bridge is supported by a strong cast-iron plate, called, as usual, the bridge-plate (fig. 54.) At the opposite end of the furnace are two rectangular flues, that nearest the back larger than the other (figs. 53, 54, 57). The object of this difference is, it is stated, to cause more flame to pass over the highest part of the bed contiguous to the larger flue. Both openings communicate with a common flue con-

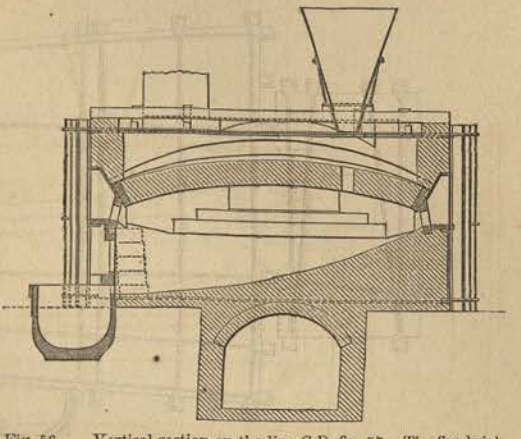

Fig. 56. Vertical section on the line C D, fig. 57. The fire-brick bearers near the fire-bridge are shown as left by the builder. Their edges soon become worn off in the course of working.

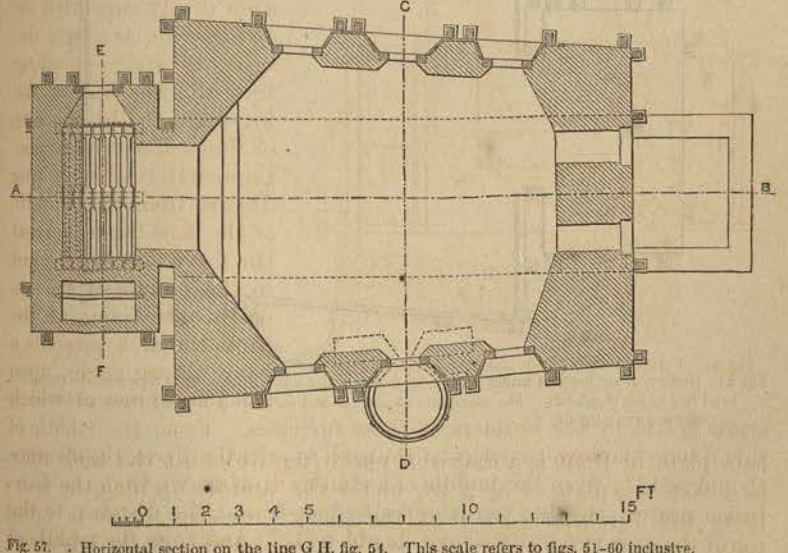

Fig. 57. Horizontal section on the line G H, fig. 54. This scale refers to figs. 51–60 inclusive.

nected with a high stack; and that flue is provided with a damper, of which much use is made when the furnace is in operation. At the flue-end on the outside there are recessed openings, corresponding to the two flues, through which access to them may be gained

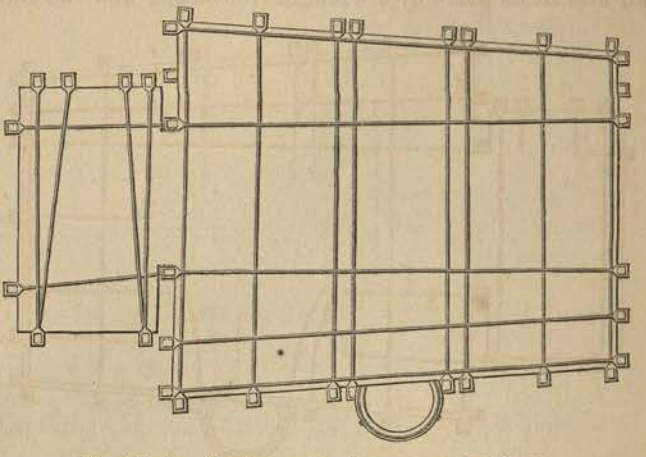

Fig. 58. Plan of the top of the furnace, showing arrangement of tie-rods.

(figs. 53, 57). They are closed with fire-brick. In the bottom and middle of each recess a little space is left in the brickwork. The furnace is stiffly braced together by wrought-iron standards and tie-rods (figs. 51, 52, 53, 54, 55, 56, 57, 58). On each side of the tap-

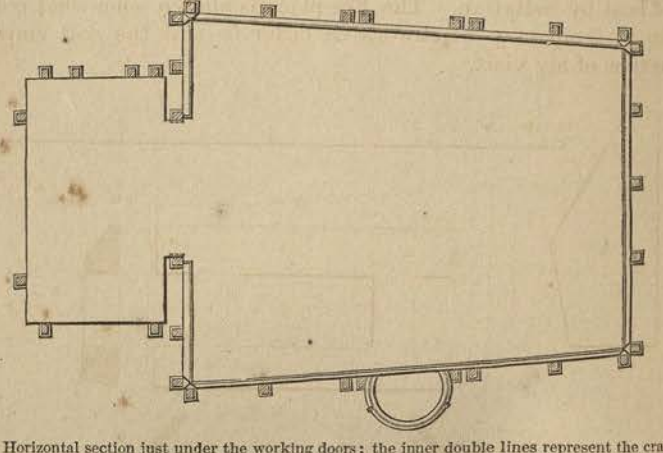

Fig. 59. Horizontal section just under the working doors; the inner double lines represent the cramping-band tied to the standards. The standards at the flue-end have been wrongly represented: they are correctly shown in fig. 58.

hole plate in front is a cast-iron plate (fig. 51). At the back there is a cast-iron plate, 4′ × 2′ 3″, under the middle opening, in order to protect the brickwork from the pasty grey-slag which is raked out through that opening; and on the floor underneath there is also a

cast-iron plate. Above and below the fire-hole is a wrought-iron plate (fig. 52). Below the flues is a cast-iron plate 5′ 8″ × 1′ 8″ (fig. 53). Many furnaces are completely cased with cast or wrought-iron plates, and those above specified are only the most essential. The lead-pot is firmly held in its place by a wrought-iron hoop; and the standards

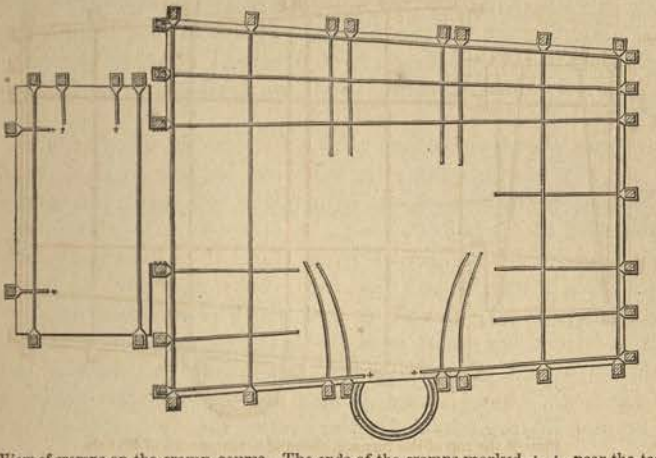

Fig. 60. View of cramps on the cramp-course. The ends of the cramps marked + +, near the tap-hole, are turned down 9″. The ends of other cramps marked + + are turned up 6″.

on each side should be let deeper into the ground than shown in the woodcuts. The space over the roof between the surrounding vertical walls is more or less filled with ashes or sand to lessen loss of heat by radiation. The fire-place is shown somewhat reduced in size by temporary brickwork in order to suit the coal employed at the time of my visit.

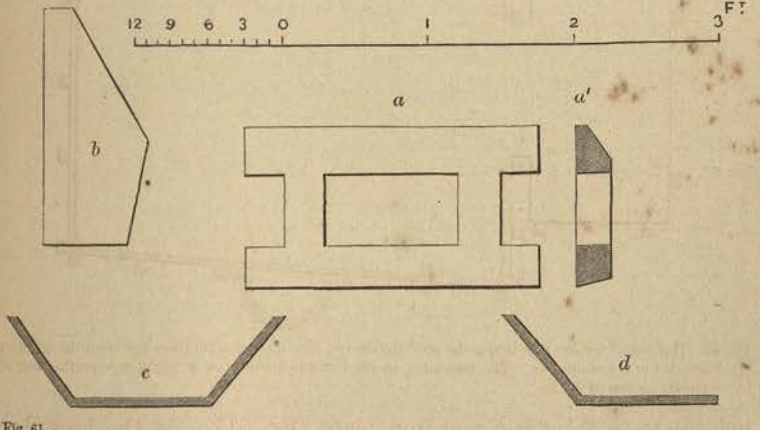

Fig. 61.

a. Elevation of door-frame.
a′. Section of door-frame, *a*.
b. Jamb-plate on the left of the first doorway at the front.
c. Plan of jamb-plates between the first and second and second and third doorways.
d. Plan of jamb-plate on the right of the third doorway at the front.

Common brick or other suitable material may be used in all those parts of the furnace—such as the foundations, exterior of the walls, crown of the air-vault, etc.—which are not to be exposed to a high temperature; but in all other parts the reverberatory lead-smelting furnaces of North Wales are built throughout of fire-bricks, made at Buckley in Flintshire, and set with the same ground clay as employed for the manufacture of the bricks. These bricks, though much less refractory than many other kinds, are well adapted for the purpose, and are even more durable in these lead-smelting furnaces than others more infusible.

The true working-bottom of the furnace is usually made in the following way of the grey-slag supplied by the furnace itself. The slag, having been broken up into pieces of about the same size as the material for road-making, is thrown into the furnace previously made red-hot, spread over the brick foundation, and then melted. When liquid it runs into the lower part or well of the furnace, where it is allowed to cool until it becomes pasty, in which state it is spread by rakes over the brick foundation, worked into the desired shape, and afterwards left to solidify by cooling. It is then ready for use. About 5 tons of slag are required for one bottom. A good bottom is important for the proper manipulation of the charge.

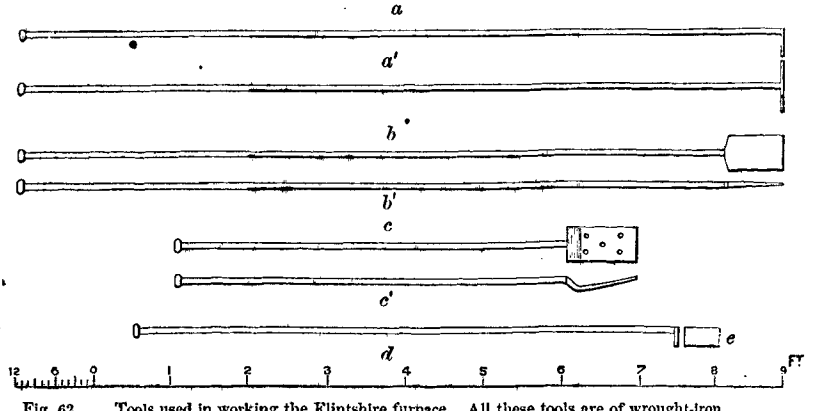

Fig. 62. Tools used in working the Flintshire furnace. All these tools are of wrought-iron.

a. Rake. Side view. Handle part 1″ in diameter, and round to the length of 3′, the other part 1″ square. The scraper part, or head, ⅜″ thick.
a'. Rake. Plan.
b. Paddle. Plan. Handle part 1″ in diameter, and round to the length of 3′, the other part 1″ square. The flattened end is tapered off to ¼″ in thickness.
b'. Paddle. Side view.
c. Skimmer. Round, 1″ in diameter in its whole length to the flattened-out part, which has five holes punched in it.
c'. Skimmer. Side view.
d. Small rake. Round, 1″ in diameter in its whole length to the scraper end, which is ⅜″ in thickness. This smaller rake is introduced through the hole in the tap-hole plate for cleaning the surface of the metal in the tap-hole after "setting up," and before tapping.
e. End view of *d*.

The paddles and rakes used on the tap-hole side of the furnace, *i.e.* the front, are 10′ long, as shown above; but those used on the opposite side of the furnace, *i.e.* at the back, are only 8′ long, as the workman on this side does not need them so long, except the rake with which he draws out the slag, and which is rather longer: the head of this rake is as large as can be conveniently passed through the doors; it is 9″ wide, 4½″ deep, and ⅜″ thick; the heads of the rakes used at the back of the furnace are 6″ wide, 4½″ deep, and ⅜″ thick. Besides the tools above described, which are the principal, there are pokers, shovels, &c., the shapes of which are not material; indeed, scarcely two tools are identical in form. The tools are generally round where the workman handles them, but square where they rest on the iron plate forming the bottom of the working doors of the furnace. Including duplicates, each furnace is provided with about sixty tools.

and any defects in it, after each tapping of the furnace, are repaired with portions of slag from the preceding charge. This true working or slag bottom varies in thickness from 6 to 12 inches, being thickest towards the tap-hole or well of the furnace and thinnest on the higher portions. I had the opportunity at Bagillt of examining the bed of a furnace in process of being broken up, and I was struck with its hardness as shown under the pick-axe. Mr. Keates states that in one furnace copper ore-furnace slag has been found to answer as a substitute. Any slag will answer equally well after a while, but none are so good for first starting as *grey-slags*.[1]

In the course of smelting, after a year or two, the furnace becomes more or less distorted in form, and consequently modified in dimensions; yet it may do its work in a manner every way satisfactory. There is no doubt that there has been in many instances over-refinement, I may even add, affectation, as to precise measurement of furnaces. Furnace-builders, like many other men of the same type, having inherited certain rules as to construction, are apt to over-estimate their importance; and the smelters themselves are sometimes not a whit the wiser than those men. However, I have endeavoured to present accurate delineations and descriptions of what I have seen and carefully examined, not that I believe in the miraculous virtues of inches in such furnaces as those used in Flintshire or elsewhere for smelting lead.

Lead-smelting in the Flintshire Furnace at Bagillt, near Holywell, Flintshire, 1859.

For the following general description of the process of lead-smelting in North Wales, I am indebted to Mr. Keates, formerly one of the proprietors of smelting works at Bagillt, near Holywell, Flintshire, and to Mr. John Henry, the manager.

The usual charge for a furnace, such as has been described and illustrated, is 21 cwts. of ore, with draughtage calculated to cover the moisture in the ore. The furnace being barely red-hot after working off the previous charge, the ore is let fall from the hopper or bin through the hole in the arch underneath, spread pretty evenly over the bed—care being taken to prevent any of it from dropping into the deepest part or well of the furnace—and frequently stirred and turned over for two hours. During this operation the temperature in the furnace is regulated by the damper, and the doors are left open, or only partially closed, in order to admit the requisite quantity of air. Constant stirring, and the highest temperature compatible with the absence of pastiness or clotting, are the essential conditions

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[1] It is reported that in Belgium furnace-bottoms of the following construction have answered well. On the top of the arch, under the bottom, a second inverted arch is built, having nearly the same concavity as the bed, and covered successively with a layer of brasque 0·25 metre thick (9·84″), a layer of blast-furnace (iron) slag 0·15 metre thick (5·91″), and a very thin layer of grey-slag containing 20% of lead. Cahen, Revue Universelle, 1863, 13. p. 13.

of this stage. If the temperature falls too low the calcination is delayed, and if it rises too high the charge is melted too soon. At the end of the two hours the grate is freed from clinkers and filled with coal, and the fire urged until the charge becomes semi-liquid; and any portion of it which may have run down towards the tap-hole is raked up to that which remained on the upper part of the furnace-bed. The fire-door is now opened, and the temperature lowered until the charge acquires the consistency of stiff paste, when the whole of it is pushed towards the bridge and back part of the furnace, *i.e.*, opposite the tap-hole side. This done the fire-door is closed, and the charge is melted down as quickly as possible into the well, slaked lime in powder is then thrown in and well raked over the surface of the melted mass. The slag and unreduced portion of ore being thus rendered sufficiently stiff, are again thrown up, or, as it is termed, "set-up," on the sloping sides of the bed, there left to cool a little and afterwards re-melted. Lime is again added, the slag is pushed back from the surface of the lead, and left to drain a little, the lead is tapped, and the slag is then raked out of the furnace in pasty lumps, termed "grey-slag."

Such is the process followed as the rule; but variations of temperature and manipulation are required to suit particular ores. The time usually occupied in working off a charge is five hours; but it may vary with the draught of the furnace, the quality of the fuel, or the nature of the ores; and when these circumstances are unfavourable, it may be protracted to six hours.

Rapid fusion of the set-up charge lessens the loss of lead by volatilization; and hence a quick, lively coal in pretty large lumps is preferred, and a furnace of such size and shape as to admit of its being rapidly cooled and rapidly heated. The more satisfactorily the calcination or first stage of the process is conducted, the greater will be the yield of the furnace, and the more nearly will it approximate to the assay-produce of the crucible. The hardening effect of slaked lime is partially due to cooling caused by the evaporation of its water.

The quantity of fuel consumed in working off a charge of ore will vary with many circumstances, the two principal being its quality and the quality of the ore. The minimum of coal may be estimated at 12 cwts. and the maximum at 16 cwts.

Two men or smelters, one subordinate to the other, are constantly required in working a furnace; and the assistance of a labourer is needed in the various attendant operations. Thus if 40 smelters are at work, not fewer than 20 labourers will be necessary. The time required to work off two charges is a shift.

A charge of about 21 cwts. of good Flintshire lead ore yields about 14½ cwts. of lead; and of this quantity about 91% of the lead is obtained direct from the furnace, and 9% from the slag and fume.

The ores treated are of high produce, yielding by dry assay from 75% to 80% of lead.

ANOTHER DESCRIPTION OF LEAD-SMELTING IN THE FLINTSHIRE FURNACE.

The next general description is from the pen of a practical lead-smelter well informed in the science of his art.

The charge consists of 21 cwts. It is spread evenly over the bed of the furnace, and calcined for about an hour and a half, being turned over very frequently.

The grate is then cleared from clinker formed whilst melting the previous charge, coal is thrown on the fire, and the damper opened a little, so as to expose the charge to a higher calcining heat, for about an hour.

More coal is then thrown upon the fire, and the doors of the furnace are closed till the charge has melted. This takes about half an hour.

The doors are opened, and a few shovelfuls of lime are thrown upon the charge to thicken the unreduced portion, which is then set-up, allowed to cool considerably, well worked, so as to divide it as much as possible, and calcined for about an hour.

The fire is again charged, the damper raised, and the doors of the furnace are closed till the charge has again melted, which requires about a quarter of an hour. It is again thickened with lime and set-up, worked, cooled, and calcined as before, but this time, as the charge is less in bulk, the calcination lasts only about half an hour.

The fire is again made up and the doors closed, till the whole charge is thoroughly melted; this takes about half an hour or rather more. (During this firing a little coal-slack is sometimes added.) The doors of the furnace are then opened, the slag again thickened with lime, and the furnace tapped. The slags are raked over the back of the furnace, quenched with water, and wheeled away.

The next charge is at once let drop from the hopper where it had been placed whilst working the previous charge. It is spread uniformly over the furnace bed, when calcination commences and is continued by the heat of the furnace walls, and what little fuel remains in the grate: if necessary a little more is added.

Whilst removing the slag and spreading the charge, a scum rich in sulphide of lead forms on the metal in the pot. It contains much lead mechanically intermixed, which is chiefly got rid of by the following method. The workman plunges a paddle into the lead and stirs the whole vigorously, then throws some coal-slack into the pot, and again stirs. This generates a large volume of gas, which he ignites by throwing into it a shovelful of hot cinders. The surface is thus thoroughly heated, and he at once returns the skimmings into the furnace, lades the lead into pigs, again taps the furnace and allows the lead which has run out from the skimmings to remain in the pot till the next charge is let into it. The tap-hole is then stopped up.

Sixteen charges of ore produced in a trial 11 tons 5 cwts. of lead and 2 tons exactly of slag, containing about 55% of lead. About 10 cwts. of fuel were employed per charge. The total loss may be taken at 5% on the lead, as shown by our method of assaying in the

iron-dish, which, when operating on such rich ores, gives results very near those of the other methods, in which fluxes are employed. This loss includes the loss in smelting the slags, and does not include the lead which will be recovered from the flues. This, however, is but a small item, and will not affect the loss more than a fraction of a per cent., unless a good condenser is used.

The following results as to the proportion of grey-slag have been communicated to me by a practical smelter. The average content of lead in 138 tons of slag (1 ton = 2240 lbs.) found by assay in the iron-crucible, with the addition of black-flux, was 55½%; and the average quantity of slag per charge on a week's work was 2 cwts. 3 qrs. The average quantity of grey-slag from the smelting of galena, yielding by assay in the iron-dish 77½%, was 2 cwts. 3 qrs. 21 lbs. per charge, which slag by assay in the iron-crucible, with the addition of fluxes, gave 53¾% of lead. About 3 cwts. 3 qrs. 16 lbs. of grey-slag were produced per charge of 21 cwts. in the smelting of an ore yielding 77% of lead, by assay in the iron-dish.

The lead from the grey-slag was formerly extracted by smelting in small blast-furnaces, called slag-hearths, but the reverberatory flowing-furnace is now commonly substituted for that purpose, and the process will be hereafter described.

Description by the Author of Lead-smelting in the Flintshire Furnace near Holywell, Flintshire.

By way of special illustration I give the following narrative of what I saw done in the working of a furnace at one of the largest smelting works in North Wales. A mixture of the best ores of 81% produce by dry assay in the iron-dish was the subject of treatment.

The charge was 21 cwts. (1 cwt. = 112 lbs.) dry, or 21½ cwts. in reality, ½ cwt. being allowed for moisture. Two men were engaged at a furnace, one on each side, *i.e.* back and front. The furnace was in full working order and much cooled down, as usual after the smelting of the last charge.

At 3 h. 40 m. P.M. the charge was let fall through the roof from the hopper and spread over the upper part of the bed. All the side-doors, as well as the fire-door, were open.

5 h. 10 m.—The first stage or *calcination* was now completed; during the whole of this stage the damper was kept down considerably. The two doors on each side furthest from the fire were now closed, while the other two side-doors were left open. The fire was well made up and the fire-door closed. Lead was observed to trickle down.

6 h. 35 m.—The fire was kept well up; the two doors nearest the fire were still left open. Rabbling was occasionally practised, first through one door and then through another. Lead trickled down pretty freely soon after the beginning of this stage.

7 h. 8 m.—All the doors on each side were closed, the fire was

well made up, and the damper raised fully. Vigorous effervescence occurred, with a frizzling sound, and lead flowed freely from the charge.

7 h. 50 m.—All the doors on each side, as also the fire-door, were opened, and the charge was well rabbled. The door on each side near the flue was closed. The charge was wholly melted down into the well of the furnace.

7 h. 54 m.—A shovelful and a half of slaked lime was introduced on the tap-hole side and well mixed with the molten mass on the top of the lead by rabbling through the tap-hole door, which was afterwards closed. Matter adhering to the sides of the bed was detached by the paddle, and raked up towards the fire-bridge by the man on the opposite side of the furnace. The flue-door on each side was still kept closed, the fire-door remained open, and the damper fully up.

8 h.—A paddle was put in through the working side (*i.e.* the back), and used to detach as well as practicable from the sides of the bed the less fused and more adherent part of the charge; and the man on the opposite or tap-hole side (*i.e.* the front), at the same time constantly used his rake for the like purpose. The matter so detached, as well as that thickened with lime on the surface of the lead in the well, was raked or "set-up" on the sloping part of the bed, near the fire-bridge. After this "setting-up" the door on each side near the fire and the fire-door were left open.

8 h. 18 m.—The damper was lowered, the fire-door closed, and the door on each side near the fire left open.

8 h. 47 m.—The damper was raised, the fire was well made up, and all the doors were closed.

8 h. 54 m.—On looking through the narrow tap-hole door vigorous effervescence, amounting to ebullition, was observed.

9 h. 12 m.—The fire-door and the two doors on each side nearest the fire were opened. The charge was well melted. Two shovelfuls of slaked lime were thrown in through the middle door on the tap-hole side, and well rabbled into the molten mass. The surface of the lead was cleared by pushing the thickened matter on its surface with the paddle from the tap-hole, as well as through the narrow door above the tap-hole.

9 h. 17 m.—The tap-hole was opened, and after the lead had run into the pot the thickened matter or "grey-slag" was raked out through the middle door and fell on an iron plate on the floor below. The damper was still up, and the furnace cooling preparatory to the next charge.

9 h. 25 m.—Another charge was let down and spread over the bed by the man on the working side, or side opposite the tap-hole. The damper was then lowered. [It should have been lowered sooner, but the workmen find it cooler to keep it up a while. This practice is contrary to orders. Slime-ore is carried away by the draught.]

9 h. 29 m.—The lead tapped off in the pot was skimmed by perforated flat iron shovels. Coal-slack and ignited coal from the

furnace were thrown on the top of the skimmed lead and well stirred in.

9 h. 32 m.—The coal-slack, &c., was skimmed off, and the skimmings put back into the furnace. Some lead sweated out and was tapped off in a few minutes afterwards. The tap-hole was stopped by throwing in a lump of thick lime-mortar through the narrow tap-hole door and then ramming from the inside, which was easily done by a bent tool.

It must be clearly understood that the manipulation, &c., varies with different ores. I simply recorded minutely what I observed at the time under the circumstances.

Analytical Data concerning Lead-smelting in the Flintshire Furnace.

The smelter whose description has been given at p. 231, was so obliging as himself to procure for me samples of charges of ore—similar to that of which I have just presented an account of the treatment from my own observation—from each charge at different stages of the process in the same furnace worked off every day consecutively during one week, as he could not trust the men to take samples in his absence during the night. These samples may, therefore, be regarded as accurately representing the mean composition of the charges at different stages of the process.

Composition of the Ore.

Sulphide of lead	89·95
Sulphide of zinc	0·99
Protoxide of lead	5·15
Lime	0·65
Sesquioxide of iron *	0·29
Alumina	0.13
Carbonic acid	1·62
Residue insoluble in hydrochloric acid	0·85
	99·63
Metallic lead	82·71

* The iron was present in the ore chiefly as bisulphide, and partly as metal, derived from the miners' tools.

The insoluble residue consisted chiefly of silica in the state of sand. Fluorine was sought for but not detected. The analysis was made in my laboratory by Mr. C. Tookey. Supposing the protoxide of lead and the lime to exist as carbonates, the former would require 1·02 and the latter 0·51 of carbonic acid. Total carbonic acid = 1·53. The quantity of carbonic acid found = 1·62. Difference = 0·09, which is within the limit of error tolerated in analysis, where so small a proportion of carbonic acid is present.

TABLE SHOWING THE COMPOSITION OF THE CHARGE OF ORE AT FOUR STAGES OF THE PROCESS AND OF THE GREY-SLAG. THE ORE WAS INTRODUCED INTO THE FURNACE EACH MORNING AT ABOUT 9½ A.M.

Number.	I.	II.	III.	IV.	V.
Time when the sample was taken.	11 A.M.	1 P.M.	1·45 P.M.	2·15 P.M.	After tapping.
Nature of the product.	Calcined ore.	Roasted ore.	After setting-up with lime.	After setting-up with lime and roasting.	Grey-slag.
Sulphide of lead: Lead	55·25	46·16	21·44	3·77	0·78
Sulphide of lead: Sulphur	8·57	7·16	3·32	0·58	0·12
Sulphide of lead: Lead + Sulphur	63·82	53·32	24·76	4·35	0·90
Sulphate of lead: Protox. of lead	2·42	3·52	5·11	10·32	7·25
Sulphate of lead: Sulphuric acid	1·00	1·26	1·83	3·70	2·60
Sulphate of lead: Protox. + Sulphuric acid	3·42	4·78	6·94	14·02	9·85
Protoxide of lead	27·25	31·49	43·12	47·50	48·87
Oxide of zinc	1·25	3·00	5·02	5·72	7·52
Lime	1·32	2·14	7·38	11·51	12·68
Alumina	0·37	0·58	1·38	1·97	3·01
Sesquioxide of iron	0·51	0·96	1·57	2·28	2·86
Silica combined*	..	..	8·32	11·04	12·52
Residue insoluble in hydrochloric acid: Silica			0·43	0·24	0·53
Residue insoluble in hydrochloric acid: Lime			0·15	0·06	trace
Residue insoluble in hydrochloric acid: Alumina and sesquioxide of iron	1·60	3·99	1·12	0·80	1·45
Residue insoluble in hydrochloric acid: Total			0·54	0·50	0·92
	99·54	100·26	99·61	99·19	99·66
Total metallic lead	91·36	78·66	66·22	47·86	52·88

* Separated by hydrochloric acid in the gelatinous state.

The analyses were made in the Metallurgical Laboratory: Nos. I., II., III., IV. by Mr. W. Weston, now Chemist at Portsmouth Dockyard, and No. V. by Mr. C. Tookey, lately assayer at the Hong Kong Mint.[1] In Nos. II., III., IV. there was a little metallic lead, which admitted of being passed through a fine sieve, and it was accordingly included in the sample prepared for analysis. Many experiments were made with a view to an accurate quantitative determination of this metallic lead, but without success. The problem, it is to be hoped, is capable of satisfactory solution. The quantity, however, was not sufficient materially to affect the conclusions stated further on. The sulphur present as sulphide and sulphuric acid was not proved to be wholly in combination with lead and protoxide of lead respectively; and accordingly in the Table the quantities of sulphur found to exist in the state of sulphide and sulphuric acid are given as well as the equivalent proportions of lead and protoxide of lead required to form sulphide of lead and sulphate of protoxide of lead. The iron is estimated as sesquioxide, though it is certain it could not have been wholly in that state; its quantity is so small that it may in this case be disregarded.

CONCLUSIONS FROM THE PRECEDING ANALYTICAL DATA.

The large proportion of lead left unreduced in the grey-slag should be specially noted. Much more lead is oxidized than suffices for the reduction of the sulphide, which, at the end of the operation, almost totally disappears. Reduction occurs in a sensible degree before

[1] He is now assayer at the Japanese Mint, Osaka. (May, 1870.)

melting or firing down the charge and before the first setting-up, but it takes place most actively during the *first* firing down of the charge, and after that period towards the completion of the process. Such are the observed facts, and they agree with the conclusions arrived at on comparing the quantitative relation between the total metallic lead and one of the fixed and invariable constituents of the charge, say the oxide of iron or alumina.

What seems remarkable is, that in the product No. II., which had been calcined at a higher temperature or roasted for some time after the completion of the first stage (to which the term calcination is restricted) and had been subsequently melted down, so large a proportion of sulphide and oxidized compounds of lead should co-exist. Probably this may in part be explained by the solution or absorption of sulphide of lead by the reduced lead with which it comes in contact, whereby it may be more or less protected or temporarily withdrawn from the reducing action of the supernatant oxidized compounds of lead.[2] The lime is added in the state of hydrate, and tends to thicken the molten mass, partly by the cooling effect consequent on the evaporation of its water, and partly by its intermixture as an infusible ingredient. When thus thickened the mass may be raked up on the higher part of the bed of the furnace, and there present an extensive surface for renewed oxidation, while at the same time opportunity is afforded for the draining off or liquation of the metallic lead which it may contain, as it were, entangled.

But may not the action of the lime be chemical as well as mechanical? It certainly exerts no sensible reducing action on the sulphide of lead; for when mixed with that sulphide and exposed to a high temperature in a brasqued crucible—that is, under conditions much more favourable to the reduction of oxide of calcium, and, consequently, to the formation of sulphide of calcium, than exist in the highly oxidizing atmosphere of the Flintshire reverberatory furnace—the sulphide is very imperfectly reduced with the production, according to Berthier, of double sulphide of calcium and lead. And it is clearly to the combination of the calcium of the lime with the sulphur of the sulphide of lead that any reduction of the latter by the former can be effected.[3]

It is conjectured that the action of the lime is chemical. May it not serve to displace protoxide of lead from its combination with sulphuric acid and so facilitate the reduction of the lead of the sulphate of lead, as the reduction of the sulphide of lead is more readily effected by free, than by combined, oxide? By reference to the foregoing Table it will be seen that there is much less sulphuric acid in

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[2] Dick states that after firing down, the melted charge cannot be left long enough in the tap-hole for complete reactions, because the furnace-bottom would melt. Hence it is necessary to thicken the remaining oxides and sulphides with lime, and set up the charge in order to prevent the destruction of the furnace-bottom.

[3] When a mixture of galena and lime is heated to redness with access of air, sulphate of lime is stated to be formed. See p. 55 antea.

the grey-slag, No. V., than in the product No. IV., from which that slag is derived. In this consideration we may ignore the presence of the oxides of zinc, iron, and aluminium; for sulphates of those metals could not exist at the temperature prevailing in the furnace towards the conclusion of the process. The sulphuric acid, therefore, recorded in Nos. IV., V., must have been combined either with protoxide of lead or oxide of calcium, or partially with both. If it had been wholly in the state of sulphate of lime, its decrease in the passage of No. IV. to No. V. is not accounted for, unless it be supposed that the silica present came into action; for silica at a high temperature decomposes sulphate of lime with the formation of silicate of lime and the evolution of sulphuric acid. But as there was present a large proportion of the strong base, protoxide of lead, which so rapidly combines with silica at a bright red-heat, it cannot be inferred that the loss of sulphuric acid in question is due to the decomposition of sulphate of lime by silica; and if this be admitted, that loss may be accounted for by the reducing action of the residual unchanged sulphide of lead upon the sulphate of lead which is supposed to be present. Now, by deducting 0·9 of sulphide of lead computed to be present in the grey-slag from 4·3 of sulphide in No. IV., the quantity is 3·49; and this quantity requires 4·4 of sulphate of lead for its complete reduction; and it is a singular coincidence, if nothing more, that this is very nearly the difference between the quantities of sulphate of lead computed to exist in No. IV. and No. V., the grey-slag. This argument, founded to a certain extent on assumption, which however on *à priori* chemical grounds seems probable, points to a negative answer to the question proposed, namely, whether the lime may act by displacing protoxide of lead from its combination with sulphuric acid. It should be particularly noted that the language here used is guarded and qualified. Further and not easy investigation is required in order to obtain such an answer as not to admit of dispute.

In the products Nos. III., IV., V., combined silica appears in sensible proportion. From No. I. to No. V. the silica has relatively increased about eightfold per cent., and another of the fixed constituents, alumina, in the same ratio; and in No. V., the grey-slag, nearly the whole of the silica is in combination. The oxygen in the bases represented as uncombined in the Table, and that of the combined silica, is as under:—

		Oxygen.	
Protoxide of lead	48·87	3·54	
Oxide of zinc	7·52	1·48	
Lime	12·68	3·61	10·90
Alumina	3·01*	1·41	
Sesquioxide of iron	2·86	0·86	
Silica	12·52	...	6·50

The ratio between the oxygen of the silica and that of the bases is nearly as 3 : 5. But simple inspection of grey-slag shows that it is not homogeneous; and when we reflect that it is the product of rabbling the molten mass in the furnace with lime not followed by

complete fusion, it is inconceivable that it should be other than a mechanical mixture, at least in a great degree, so far as the lime is concerned. Supposing the whole of the lime to be free in the grey-slag, the oxygen of the silica and that of the remaining bases would be nearly in the ratio of 3 : 3, *i.e.* the same as exists in tribasic silicates. But much of the oxide of lead in silicate of lead so highly basic would act upon sulphide of lead nearly, if not quite, as easily as if it were uncombined. The addition of lime, therefore, is not needed to set free oxide of lead from its combination with silica in order that it may reduce sulphide of lead.

Now, if lime does not act by displacing oxide of lead from combination either with sulphuric acid or with silica, how otherwise can it exert chemical action? I am unable to suggest an answer; and so far as the analytical data in the Table are accepted as sufficient for reasoning on this interesting subject, the action of the lime would seem to be mechanical. By the addition of that substance, the molten mass in the furnace, floating it should be remembered on the liquid lead already reduced, is thickened so that it can be "set-up," drained of lead which it may contain entangled, and exposed over a large extent of surface to oxidation. But in this operation of "setting-up" the bulk of reduced lead becomes likewise exposed to the oxidizing influence of the air, and may so be freed in a greater or less degree from sulphide of lead with which, especially towards the upper part, it may be contaminated. The large excess of residual oxidized compounds of lead is desirable in order to lessen the quantity of the sulphide dissolved in or intermixed with the reduced lead, and which otherwise would flow out with the latter through the tap-hole. Lead saturated with sulphide of lead would form a pasty mass and set like solder on cooling.

Observations of my friend, Mr. Dick, whose name has so often appeared in the preceding volumes of this work, seem opposed to the view that the action of the lime is exclusively mechanical. He informs me that he has repeatedly noticed that immediately after the lime is thrown into the furnace, preparatory to the *first* setting-up, the mass with which it intermingles appears, as it were, to burn like tinder, beginning at one part and quickly extending thence over the whole surface. He has never noticed any sign of chemical action after the addition of lime preparatory to the *second* setting-up, in which stage of the process he considers its action to be wholly mechanical or nearly so. As Mr. Dick has during many years been attached to some of the largest lead-smelting works in the kingdom, as he assures me he has seen this phenomenon when he looked for it, and as I know him to be a most careful and trustworthy observer, these results of his experience deserve much consideration. They indicate, but do not demonstrate, chemical action. I am unable, however, at present to interpret their meaning.

The question may be put, Why use lime in this process if its action be wholly mechanical? Let any one try to suggest a substitute which would answer equally for this purpose, and if I mistake

not, he will be not a little puzzled. Moreover, it may be valuable as a slag-forming ingredient in the subsequent extraction of lead from the grey-slag, which is attended with perfect fusion.

It will be remarked that zinc is not sensibly reduced in this process, as might have been anticipated.

The entire process may be divided into four operations as follow:—

I. Calcination at a comparatively low temperature.

II. Raising the temperature so as to melt the calcined product, whereby considerable reduction of lead occurs by the reaction between the unchanged sulphide and oxidized compounds of lead in the calcined product.

III. Setting-up with lime and completion of the reduction of the residual sulphide with the generation of a much greater quantity of oxidized compounds of lead than suffice for the reduction of that sulphide.

IV. Tapping out the reduced lead, and afterwards drawing out the grey-slag in pasty lumps.

In metallurgical books which treat of the process of lead-smelting in the reverberatory furnace, oxysulphide and subsulphide of lead are made to play an important part. I have ignored both, first, because I have not met with satisfactory proof of the generation of such a compound as oxysulphide of lead in the furnace; and secondly, the formation of subsulphide of lead has not been certainly established, and if it had been, its reduction by means of oxidized compounds of lead would be exactly analogous to that of the monosulphide.

Additional Analytical Data concerning Lead-smelting in the Flintshire Furnace.

Composition of the Products of Smelting Galena in the Reverberatory Furnace at the Lead Works of Messrs. Newton, Keates and Co., Bagillt, near Holywell, Flintshire, furnished to the Author by Mr. Keates, and the manager Mr. John Henry, 1859.

I.				II.	III.
Ore calcined for 2 hours after its introduction into the furnace.				Product 3 hours after introduction of ore into furnace.	Grey-slag after tapping.
Sulphide of lead	Lead	46·57	53·79	47·23 / 7·33	54·56	...
	Sulphur	7·22				
Sulphate of lead	Protoxide of lead	2·09	2·84	5·64 / 2·03	7·67	13·80 / 4·93	18·73
	Sulphuric acid	0·75				
Protoxide of lead			36·87	27·18		38·08
Oxide of zinc			2·65	5·19		12·00
Lime			1·63	1·96		13·50
Protoxide of iron			0·90	1·33		3·89
Alumina			...	...		0·71
Silica			1·10	1·85		12·32
			99·78	99·74		99·23

These analyses were made in the Metallurgical Laboratory by Mr. W. Weston. Nos. I., II., correspond to the products under the same Nos. in the preceding Table, and No. III. to No. V. in that Table. The similarity in composition is striking; but the ore operated upon was probably the same as that referred to in the preceding Table at p. 234.

Lead-smelting in the Flintshire Furnace at Alport, Derbyshire.

The lead-smelting works at Alport belong to Messrs. Barker and Rose, to whom I am indebted for the information concerning charges and yields. The furnace is similar in construction to the furnaces at Holywell, but is smaller, and has two tap-holes, one for lead and the other for slag. The length of the bed from the fire-bridge to the opposite end is 10′; the breadth at the doorway near the fire-bridge is 8′, and at the doorway near the flues 7′ 5″; the grate is 4′ 3″ long and 2′ wide; the fire-bridge is 2′ 6″ wide; the distance from the top of the fire-bridge to the arch above it is 1′ 5″; the six side doorways are of the same size, 11″ wide and 7″ high; the lead-pot is 1′ 10″ in diameter, inside measure. The average produce of the ores, as determined by assay in the iron-crucible, is from 76% to 77%. The charge is 16 cwts. of ore, and each charge is worked off in from 4½ to 5 hours. The yield of lead is from 71% to 72%. The slag is *tapped off*, and amounts to 3¼ cwts. per charge: the proportion of lead which it contains is variable, but it yields by assay on the average from 6% to 8% of lead: a small quantity of *drawn-slag* is occasionally produced. Lime is employed in "setting-up." The lead is tapped out after the slag has run out. Fluor-spar is added as a flux in the smelting of ores containing much sulphate of baryta. The loss of lead is variable, but is stated to be 5% as compared with the produce by assay. (March, 1868.) The slag is treated in a Spanish Slag-Hearth, and the fume is collected in a special condensing arrangement, both of which will be described in due course. (See p. 418 and p. 438.)

The manner of conducting the process is essentially the same as that at Holywell, with the exception that the slag at Alport is liquefied and run out of the furnace, instead of being drawn out in pasty lumps. This difference is due to the nature of the matrix or vein-stuff of the Derbyshire ores, which usually contains sulphate of baryta or fluor-spar in considerable quantity; and these two substances when intermixed readily melt into a thinly liquid product at the temperature prevailing in the furnace. (See First Part of this work.) Run-slag is compact, opaque, earthy in fracture, and yellowish or brownish-grey. It was formerly termed "macaroni-slag," and thrown away or used in road-mending.[1]

I have not met with the record of analyses of such slags more recent than the following of Berthier.[2] He operated upon specimens

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[1] Forster's Section of the Strata, etc., antea cit. p. 375.

[2] Voyage Métallurgique en Angleterre, 2nd ed. 1839, 2. p. 662.

from the Lea Smelting Works near Matlock. The ore is described as of two kinds, pure galena and galena mixed with carbonate of lead and sulphate of baryta. A specimen of the latter was composed as follows:—

Galena	55
Carbonate of lead	23
Sulphate of baryta	19
Clay	3
	100

The two kinds of ore were mixed and smelted together in equal proportions of each, the charge being 16 cwts. A flux consisting of 75% of fluor-spar and 25% of calc-spar was added. Two kinds of slag were produced, one which was *run* out, and the other less fusible, which remained on the bed of the furnace and was *drawn* out. As Berthier suggested, when carbonate of lead and sulphate of baryta are present, it would not be possible to separate the latter from galena by dressing without risking sensible loss of the former.

Composition of Run-Slag.

	I.		II.
Fluoride of calcium	16·0		13·6
Sulphate of baryta	25·0		30·0
Sulphate of lime	22·5		33·0
Sulphate of lead	22·0		9·0
Oxide of iron	4·5		2·0
Oxide of zinc			2·0
Lime	8·0		8·8
Carbonic acid and loss	2·0		1·6
	100·0		100·0

These slags were compact, very light grey with a slightly yellowish tinge, shining in the interior of cavities, granular and dull in fracture: they were occasionally mixed with small portions of regulus.

Composition of Drawn-Slag.

Fluoride of calcium	7·2		8·5
Sulphate of baryta	22·0		24·4
Sulphate of lime	1·6		5·6
Sulphate of lead	12·0		30·0
Oxide of iron	15·4		5·6
Oxide of zinc	7·2		8·0
Oxide of cadmium	trace		trace
Lime	14·0		14·7
Galena	17·6		2·0
Carbonic acid and loss	3·0		1·2
	100·0		100·0

These slags were not homogeneous. The predominant substance was light-grey and dull like *run-slag;* but it was sensibly porous and mixed with white, dull, earthy particles, resembling lime, and with numerous brilliant lamellar portions, resembling galena.

LEAD-SMELTING IN THE FLINTSHIRE FURNACE IN OTHER LOCALITIES.

Tarnowitz, Upper Silesia.—The Flintshire furnace was introduced into Friedrichshütte (*i.e.* the Frederick Smelting Works), at Tarnowitz in 1862. The history of those works will be given further on in this volume in an article headed, Iron-reduction Process, to which the reader is advised to refer for information concerning the nature of the ores there treated. The ores, which will be found to consist of galena associated with carbonate and sulphate of lead in notable proportion, are passed through rolls and then through sieves with 25 holes to the square inch. The furnace is essentially the same as that of Flintshire, and differs only from the latter in having the well and tap-hole below the door nearest the flue; and the process is carried on in essentially the same manner as in this country. It is reported that, thanks to the self-education of the workmen, the charge was raised from 20 ctrs. in 1862 to 40 ctrs. in 1865. Coal from Königsgrube (*i.e.* King's Mine) is the fuel used. The calcination lasts from 3 to 4 hours, and is conducted with the usual precautions as to temperature in order to prevent clotting. A charge is smelted in about 7 hours, and lead is tapped off several times. The drawn-out grey-slag amounts to from 4 to 6 ctrs., and is stated to be composed as follows:—

COMPOSITION OF GREY-SLAG, TARNOWITZ.

Protoxide of lead	24·375
Sulphate of lead (PbO,SO^3)	13·269
Silicate of lead (PbO,SiO^2)	12·373
Oxide of zinc	22·857
Protoxide of iron	8·957
Sulphide of iron (FeS)	1·823
Lime	11·190
Carbon	4·821
Alumina, Protoxide of manganese	traces
Silver	0·015
	99·680

The grey-slag is passed through a blast-furnace.

The proportion of silver in the lead obtained at each tapping from a charge of 40 ctrs. of ore has been determined, and the results are as under:—

Order of tapping.	Weight of lead in ctrs.	Proportion of silver per cent.
1	8·80	0·1445
2	7·37	0·1210
3	5·22	0·1095
4	2·66	0·0995
5	2·13	0·1035
	26·18	Mean ... 0·12299

In the following Table are given details of the smelting during the three years 1863, 1864, 1865:—

TABULATED RESULTS OF SMELTING IN THE FLINTSHIRE FURNACE AT TARNOWITZ, 1863, 1864, 1865.

Year.	Average contents by assay.		Furnace lead.		Charge of 100 ctrs.* yielded								Lost or gone off.		In smelting a charge of 100 ctrs.		Proportions of lead and silver obtained of the total of these metals indicated by assay.	
					Grey-slags.			Fume.‡			Total.							
						Contained			Contained		Lead.	Silver. Pounds.			Coal.	Lime.		
	Lead °/₀.	Silver °/₀.	Ctrs.	Contained Silver °/₀.	Ctrs.	Lead °/₀.	Silver °/₀.	Ctrs.	Lead °/₀.	Silver °/₀.	Ctrs.	(1 ctr. = 100 pounds.)	Lead °/₀	Silver °/₀.	Ctrs.	Tonnen.†	Lead °/₀.	Silver °/₀.
1863	69·81	0·07640	50·98	0·1370	31·75	47·50	0·0180	1·06	50·00	0·0120	66·59	7·5770	3·22	0·00770	43·5	0·54	73·03	91·8554
1864	74·01	0·07341	61·00	0·1160	20·64	45·30	0·0111	1·40	50·00	0·0050	71·05	7·3121	2·96	0·00029	42·5	0·06	82·43	96·3919
1865	72·97	0·07461	63·84	0·1150	15·92	38·80	0·0135	2·75	50·00	0·0090	71·32	7·4536	1·65	0·00008	46	0·05	87·49	99·9156

In 1864 the cost in smelting, per ctr. of lead, was 7 sgr. 6·14 pf. = 8·78 pence, and, per ctr. of ore, 4 sgr. 6·98 = 5·38 pence; or about 14*s.* 7½*d.* and 9*s.* respectively per ton.

* 1 Ctr. = 110·232 lbs. avoirdupois.

† 1 Tonne = 7⅛ Prussian cubic feet = 219·846 litres.
1 Linear foot Prussian = 1·03 English, very nearly.

‡ Said to consist chiefly of sulphate of lead.

Clausthal, Upper Harz.—The smelting of galena in the Flintshire furnace has been tried at the Clausthal Silver Works, but without success; and the failure is ascribed to the large proportion of silica and alumina even in the dressed ore, often amounting to 17%. During calcination, the silica entered into combination, so that in firing down the separation of the lead was attended with the formation of a "stony mass," or slag, from which lead could not be extracted in the usual subsequent treatment. The presence of sulphide of antimony and spathic iron ore increased the evil, which, however, was in some degree lessened by mixing the ore with lime. The yield of lead from ores rich in silica was reduced to 20% or under.[3]

Adra, South of Spain.—In the Flintshire furnaces at Adra, there is no hole in the arch for charging, so that the ore is thrown in through the side doors, and the grey-slag is drawn out at the tap-hole.[4]

Brittany Furnace.

Under the name of "procédé breton," French writers describe a process of lead-smelting formerly carried on in the old province of Bretagne at Poullaouen in the Department of Finistère, and at Albertville in Savoy. The smelting works, however, in both those localities are closed; but according to Gruner, certain ores are still treated by the Brittany process near Marseilles, at Nantes, and at Holzappel, in the duchy of Nassau.[5] The mode of proceeding is nearly the same as in the Flintshire furnace, and reduction is effected on the same principle.[6] The furnace at Poullaouen differed mainly from that of Flintshire in the following respects:—There were three doors on one side, and none on the other; the bed was 3^m 33 long (12′ 11″) and about 1^m (6′ 3″) wide at the three doors respectively; it sloped gradually towards the tap-hole, which was below the middle door, as usual; it was made of clay (*argile grasse*), well beaten down and dried very slowly; it became pretty quickly impregnated with plumbiferous matters, and in a few days acquired considerable hardness, needing renewal only once a year. The charge was 1300 kil. (about 25 cwts.) of ore, which consisted of galena associated with from 3% to 4% of quartz, and from 12% to 13% of iron-pyrites and blende, and it was heated so gradually as to be only dull red-hot after the lapse of 5 hours from the beginning, the doors being left open and wood used as fuel. The temperature was then raised until the ore began to soften, when immediately it was vigorously rabbled. Then followed a second roasting for 2 hours, at a higher temperature, and rabbling, after which the lead was tapped off. What remained in the furnace was subjected to alternate roastings and rabblings for shorter periods, and at increasing temperatures. After each rabbling, the furnace

[3] Kerl's Handbuch, 2nd. ed. 2. p. 77. 1863.

[4] Petitgand, Revue Universelle, 9. p. 362.

[5] Ann. d. Mines, 6 sér. 13. p. 335, 1868.

[6] Rivot, Principes Généraux, p. 616. See also descriptions of the smelting works at Albertville by M. Replat, Ann. d. Mines, 3. sér. 18. p. 161, 1840; and 4. sér. 4. p. 331, 1843.

was tapped. Up to the time of the first tapping wood was used as fuel, but afterwards coal. About 13 hours after charging, the furnace being then bright red-hot and its contents nearly melted, pieces of wood and coal-slack were thrown in, and the rabble again energetically applied. More lead was thereby reduced and tapped off. When the fuel added for the purpose of reduction was entirely consumed, air was admitted for a few minutes through the doors, after which there was another and last rabbling at bright-redness. The slags were drawn out through the two side-doors and cooled with water. The time required for smelting the charge was about 16 hours. The lead was skimmed, "poled," skimmed again, and laded into pig-moulds. According to Rivot, the products obtained in smelting 100 parts by weight of ore, containing 66% of lead by assay, were 47% of furnace lead (*i.e.* 71% of the lead in the ore) and 32·4% of grey-slag, yielding by assay from 38% to 39% of lead. The loss of lead amounted to about 10% of the lead in the ore. The lead remaining in the slags was chiefly in the state of sulphate and silicate. The cost of smelting 1000 kil. (say 1 ton) of ore in the reverberatory furnace at Poullaouen was estimated at 18·6 francs, or about 14*s.* 10*d.* Rivot admitted that in the Flintshire furnace less fuel is required, owing, as he supposed, to the exclusive use of coal in that furnace; the yield is larger, and the loss of lead not so great.

Belgian Flintshire Furnace with two Fire-places.

This furnace with two fire-places, one at each end, was rectangular, but filled in at the angles with short sides as in the Flintshire furnace, which in other respects it resembled. There were three doors on each side and a tap-hole under the middle door on one side. The bed sloped in all directions towards the tap-hole, the inclination being 0·2 metre (7·87″) per metre (3′ 3·37″); it was 4·7 metres long (15′ 5·04″) and 2·9 metres wide (9′ 6·17″). Each fire-place was 2 metres long (6′ 6·74″) and 0·5 metre wide (1′ 7·69″).

Comparative trials with the same kind of galena have been made in Belgium between this furnace and what is termed the English, *i.e.* the Flintshire, furnace, and under varying conditions in the process, especially in the temperature and duration of the first stage of calcination. The results of those trials have been reported by M. Cahen in a Prize Essay entitled the Metallurgy of Lead.[7] The galena yielded 79% of lead by assay in the iron-crucible. Drawings are given of the English furnace employed, which show that it differed considerably in relative dimensions, form, and other particulars from that previously described and illustrated in this volume. The length of the bed was 2·7 metres (8′ 10·3″) and its mean width 2·9 metres (9′ 6·17″); the grate was 2·0 metres (6′ 6·74″) long and 0·5 metre (1′ 7·69″) wide; the width of the fire-bridge was 0·6 metre (1′ 11·62″), its height from the grate was 0·35 metre (1′ 1·78″), and its height from the bed 0·3 metre (11·81″); the height of the roof from the fire-bridge was 0·3 metre (11·81″).

[7] Revue Universelle, 1863, 13. pp. 1, *et seq.*

The results of the above-mentioned trials are presented in the following Table, abridged from the Table given by Cahen:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Charge .....kilogrammes	1000	1000	800	1000	1000	1600	2000	2000
Duration of a charge ..... hours	9	9	9	9	12	16	16	12
Lead obtained..... ...kilogrammes	627·7	560	468	477	630	1096	1304·4	1036
Grey-slag obtained..... id.	153	290	225	354	223	158	310	744
Lead in grey-slag..... per cent.	39	50	44	74	35	22	30	62
Lead in grey-slag.....kilogrammes	59·8	145	99	262	78	34·76	93	463
Direct yield of lead..... per cent.	62·77	56·0	58·5	47·7	63·0	68·5	65·3	51·8
Yield, inclusive of lead in grey-slag ..... per cent.	68·75	70·50	70·87	73·9	70·8	70·67	69·97	74·86
Loss of lead on 100 kilogrammes of ore	10·25	8·5	8·13	5·1	8·2	8·33	9·03	4·14
Do. on 100 kilogrammes of lead	12·97	10·7	10·3	6·45	10·4	10·5	11·4	5·2
Coal per 1000 kilogrammes kilogr.	712	562	633	506	700	917	734	375
Labour per 1000 kilogrammes of galena... francs	3·75	3·75	4·70	3·75	5·00	7·91	6·33	4·75
Smithery costs do. do. francs.	4·80	2·00	2·40	2·00	3·20	3·20	2·40	0·80

The most favourable result recorded in the Table is declared to be that in column No. VIII., in which the direct yield of lead from ore containing 79% is 51·8%, with the production of 37·7% of grey-slag, containing 62% of lead, the loss being 5·2% of lead, inclusive of what is estimated to be recovered from the grey-slag. Now, the results obtained in smelting galena in this country in the Flintshire furnace, yielding about 81% of lead by assay in the iron-dish, which have been reported at p. 232, are as follow:—the direct yield was 66·9%, with the production of 11·9% of grey-slag, containing about 55% of lead, the loss inclusive of what occurs in smelting the slag being 5%. The consumption of coal, however, was much less in the trial reported in column No. VIII. than in the English trials; but then it must be borne in mind that the direct yield of lead was much smaller, and the production of grey-slag much greater in the former than in the latter. From the preceding considerations it will be perceived that the Belgian trials in the so-called English furnace could not have been satisfactorily conducted, owing to deficient skill, to faulty construction of the furnace, or, as is possible, to both causes. The difference between the Belgian and English results cannot be ascribed to difference in the quality of the galena treated in the two cases; for we are informed that the ores of Belgium, when well dressed, are easily smelted (*sont d'un traitement métallurgique facile*), and the ore operated upon in the English trials, it is certain, was easily reducible.

SMELTING IN THE SPANISH REVERBERATORY FURNACE.

An excellent description of the construction and mode of working this furnace has been published by M. Petitgand from personal observation, of which I shall freely avail myself in the following pages, translating literally when necessary.[1] I may add that I have

[1] Exploitation et Traitement des Plombs dans le midi de l'Espagne. Par M. Petitgand, Ingénieur civil des Mines. Revue Universelle, 1861, pp. 111. The same author had previously published in the Mémoires de la Société des Ingénieurs Civils, for 1852, a paper "Sur la construction des fours à traiter le minérai de

corresponded with M. Petitgand on the subject. Mr. Joseph Lee Thomas, who officiated for some time as local mining engineer at the Linares lead-mines and smelting-works under the direction of Messrs. Taylor, has at my request furnished me with an account of these furnaces, which I shall give with but slight alteration *in extenso* and with drawings from which the accompanying woodcuts have been prepared. I have the pleasure of numbering Mr. Thomas amongst those who have attended the metallurgical course at the School of Mines.

The Spanish reverberatory furnace, *horno reverbero*,[2] has nearly always the form of a rectangular prism, and the interior, though it may vary somewhat, is always substantially the same in construction. It is called *boliche* by the Spaniards, a term indicative of smaller dimensions, but M. Petitgand, in the many furnaces which he saw, was never able to detect any difference between one furnace and another except the name. They are made of thick rubble with vegetable soil or clay for mortar. They are usually supported at the angles with solid buttresses to prevent outward thrust, and these are not unfrequently surmounted with pillars carrying the roof which covers them. Internally they have a lining of thick bricks made, as is also the bottom, of refractory clay, called *laja* or *laguena*, and resulting from decomposed talcose schists: it is variegated whitish-green, and occurs in proximity to all the mining localities in the south. Its composition is as follows:—

Silica	39·88
Alumina	15·22
Oxide of iron	25·53
Lime	3·61
Water and bituminous matters	15·47
	99·71

In spite of the large quantity of oxide of iron, bricks made from *laja* are highly refractory.

I now give Mr. Thomas's description of the furnaces at Linares in the province of Jaen, in Spain, one of the most important lead-producing districts in the world.[3]

The ore is galena and is raised from lodes which traverse the granite and yield annually about 20,000 tons and upwards. Until recently, all the ores extracted from the mines of the district were smelted in furnaces (*boliches*) of the following description, and which were first used at the Government establishment of Arrayañez.[4]

plomb employés en Espagne," p. 20. There is an interesting paper on the subject by M. Adrien Paillette, ingénieur civil, in the Ann. des Mines, 1841, 3. s. 19. p. 239; its title is, 'Sur le gisement, l'exploitation et le traitement des minérais de plomb dans les environs d'Almeria et d'Adra (Andalousie).' See also, Die Bleigewinnung im südlichen Spanien im Jahre 1829. Hausmann, Studien des Götting'schen Vereins Bergmännischer Freunde, 1849, 5. p. 221.

[2] According to Dick, "Horno reverbero" is used to designate a slight modification of the Flintshire furnace, which is employed at Adra and Berja, and occasionally elsewhere. The "boliche" is, however, essentially reverberatory in principle.

[3] Dick informs me that when he visited this locality he saw a *boliche* in operation, which had been so modified in construction as to burn coal.

[4] The following information has been supplied by Mr. Thomas:—The increase

Until very lately, the only fuel available for smelting purposes was underwood cut in the vicinity of the mines, and which consists principally of ilex and gum-cistus of about four years' growth. It is delivered at the works in its green state, and the quantity consumed of it is 90% of the weight of the ore reduced.

The furnace is represented in front and left-side elevation, in plan, and in longitudinal and transverse sections in figs. 63, 64, 65, 66, 67, respectively. It consists essentially of two arched chambers; A, a reduction chamber, and B, a second chamber, the object of which, it is stated, is to moderate the draught of the furnace; the two chambers are separated by a bridge, in which are two openings or passages, *b*, *b*.

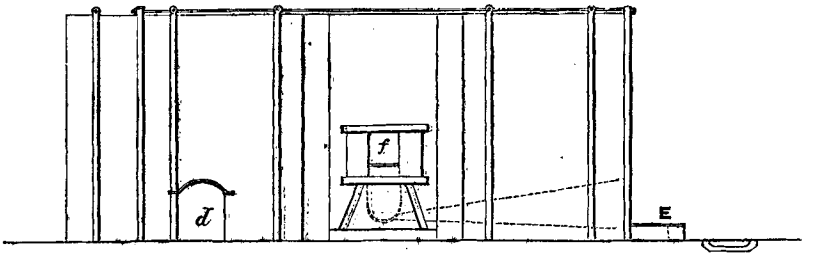

Fig. 63. Front elevation.

By means of the apertures *a a*, this second chamber may be entered when it is necessary to clean it out, or to repair the flues *b*, *b*. C is the chimney, which is usually about 30 ft. in height; latterly, however, long condensing-flues have been introduced in this district, and these short chimneys to each furnace dispensed with; D is the fire-place proper, 2′ 2″ wide and 5′ 6″ in length; there are no fire-bars, and the air required for supporting combustion is supplied by the apertures *c*, *d*, the latter specially performs this office, the air entering by the aperture *d* shown in the front elevation (fig. 63); through this aperture the embers are also raked out. The fuel is supplied to the furnace through the door *c*, formed by an iron casting shown to a larger scale in fig. 68. The furnace is only furnished with one working door, *f*, which is placed in front of it; the position of

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that has taken place during the last few years in the quantity of lead ore (galena) raised in the district of Linares is very remarkable,—in the year 1861 the production of the district was 180,064 metrical quintals, or, say, 18,006 tons,—in 1862 it was 250,901 metrical quintals, or 25,090 tons,—in 1863 it was 270,397 metrical quintals, or 27,039 tons,—and in 1866 it had reached 383,539 metrical quintals, or 38,353 tons. The figures given above, up to 1863 inclusive, are taken from statistics published by the Spanish Government, and those for 1866 from the 'Revista Minera,' and should approximate very closely to the truth. The 'Revista' says, there is reason to believe that the quantity for 1866 is understated. The number of hands employed in the mines of Linares yielding ore, *i.e.* productive mines, is given in the 'Revista' as 4241, but from this number must be deducted 175 who are occupied in extracting slags from the sites of ancient smelting operations—leaving 4066 as the number actually engaged in mining operations, and who, in 1866, raised 38,353 tons of ore, being at the rate of 9½ tons nearly for each individual engaged—a result, he believes, unprecedented in any other lead-mining district in Europe, and probably in the world.

this door, however, enables the workman to have most perfect and easy command of the charge during the process of reduction. Details of the castings pertaining to this door are shown in fig. 69, *f*. In fig. 69 is a round bar of iron or steel dropped loose into grooves in the side castings, *g*, *g*, in which it is free to revolve, as the tools used in rabbling or setting-up the charge are drawn backwards

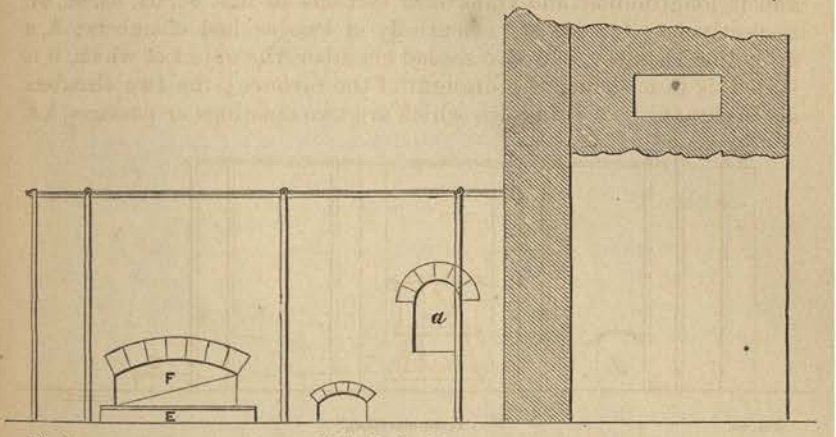

Fig. 64. Left-side elevation.

and forwards over it. *h* is a plate of cast-iron, over which the slag passes when it is raked through the door *f*. The reducing chamber, A, rises gradually from front to back, and at the lowest part, *i.e.* directly in front and immediately under the working door, *f*, is a circular cavity, *j*, 1′ 2″ in diameter, in which the fused metal collects. This receptacle is connected with a reservoir, E, by means of an arched

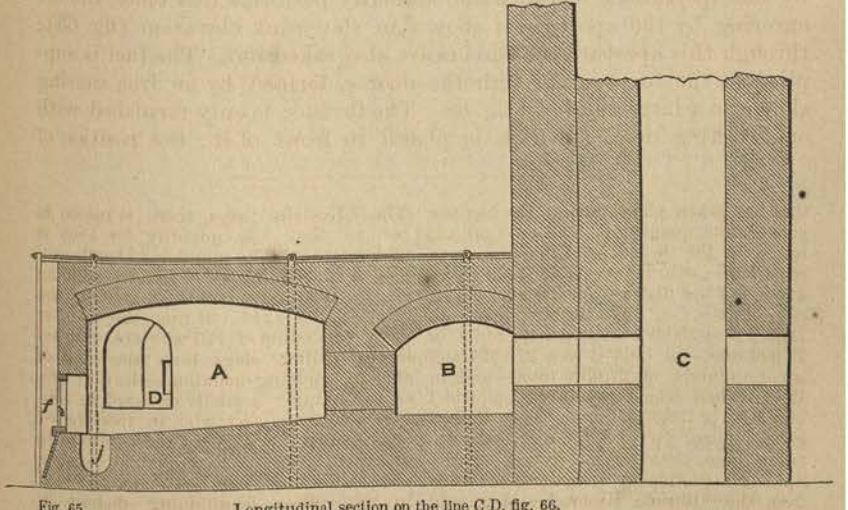

Fig. 65. Longitudinal section on the line C D, fig. 66.

recess, F, shown in fig. 64, into which the metal is tapped, and from which it flows through a piece of iron bent V shape into the moulds placed for its reception.

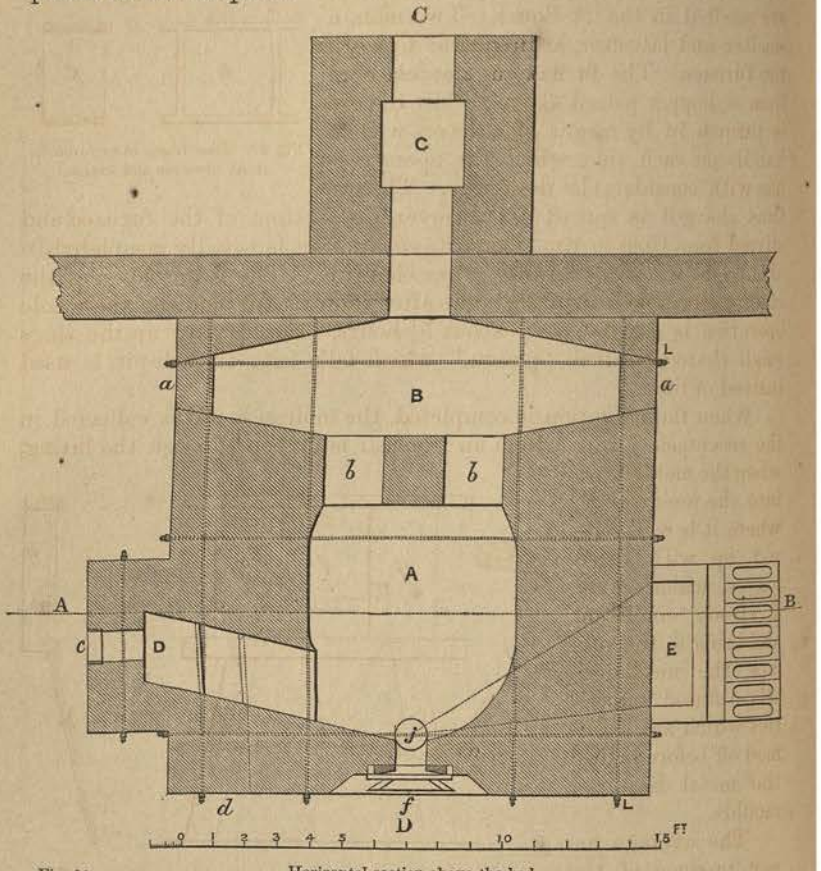

Fig. 66. Horizontal section above the bed.

The furnace above described is built entirely of a refractory sandstone, quarried in the vicinity of the mines; no fire-bricks are used in its construction; care is taken to select blocks of sandstone of some length for the exterior of the furnace. The stanchions *l l*, are of iron 2″ square, and are tied together by tie-bars of 1″ round iron; in some instances where great economy is the object, these iron stanchions are replaced by timber ones. The bed of the furnace is formed of a refractory red clay, with which is mixed a certain quantity of galena. The cost of the furnace is about 45*l.*, that of an English one in this district being about 240*l.*

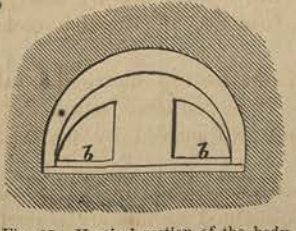

Fig. 67. Vertical section of the body on the line A B, fig. 66.

The charge of ore smelted in these furnaces is 60 arrobas = to 13 cwts. 1 qr. 16 lbs. English, and the time occupied in its reduction is 6 hours, consequently four charges, or 2 tons 13 cwts. 2 qrs. 8 lbs., are smelted in the 24 hours. Two men, a smelter and labourer, are required to work the furnace. The furnace is not charged from a hopper placed above it, but the ore is thrown in by means of a scoop with a handle on each side, which the operatives use with considerable dexterity. The ore thus charged is spread evenly over the bottom of the furnace and stirred from time to time; and its calcination is usually completed in about 1 hour and 20 minutes after charging. The firing down of the charge commences about 3½ hours after its introduction, and the whole operation is concluded in about 5¼ hours. For drying up the slags small charcoal called "piccou," which falls into the ash-pit, is used instead of lime.

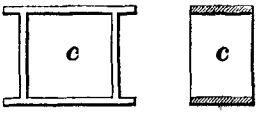

Fig. 68. Door-frame of cast-iron, in front elevation and section.

When the reduction is completed, the molten metal is collected in the receptacle *j*, into which an iron bar is driven through the luting, when the metal flows into the reservoir E, where it is well stirred up with dried leaves, which cause a strong ebullition and bring to the surface the mechanically diffused impurities which are skimmed off before lading the metal into the moulds.

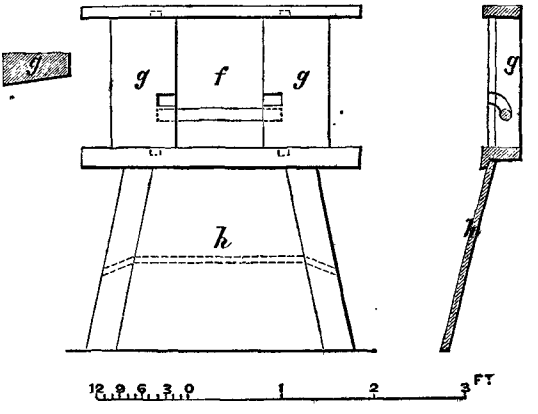

Fig. 69. Details of working door.

The average assay produce of the ores treated is 77·5%; and under favourable circumstances, *i.e.* in the dry summer weather, the yield is in the first fusion 80·5 per cent. of the contents of the ore by assay, or about 2% less than they would yield in furnaces of English construction with coal for fuel.

The grey-slag varies from 15% to 17% of the ore charged, and yields by assay from 46% to 50% of lead. It is reduced in a blast-furnace, the blast being supplied by a bellows moved by man or horse power.

The erection of a "boliche," where cheap coal and the materials necessary for an English furnace can be obtained at moderate cost, would be out of the question (at least in its present form), but in some districts this furnace, or some modification of it, may be employed with advantage. Mr. Thomas thinks this furnace might be

improved by lowering the roof and making it flatter. Almost any stone will serve for the construction of the main part of this furnace; thus at La Carolina, near Linares, where clay-slate is the prevailing rock, furnaces are constructed of it.

Dick has communicated to me the following results of his observations on smelting in a *boliche* at La Fortuna, Linares. The process was divided into three operations:—

1. *Caldeo* (from *caldear*, to heat). It is analogous to our *calcination*, and lasted from 1 to 1½ hour.
2. *Blandeo* (from *blandear*, to soften). It is analogous to our *sweating* or *roasting*, and lasted from 4½ to 5 hours.
3. *Corrida* (running, race). It is analogous to our *running down*, and occupied the remainder of an 8-hours' shift.

Before running down, the surface of the lead was carefully cleaned with carbonaceous ashes, and the grey-slag was eventually set up after intermixture with these ashes. The work was well done.

In some places, as at Arrayañez, for example, the charge is 60 arrobas, which is smelted in 6 hours with brushwood as fuel.

Boliche with brushwood as fuel.—Three charges of ore, of 86 arrobas each, were worked off in 24 hours, with a consumption of about an equal weight of brushwood. It was reported that the yield of lead was 53⅓ arrobas per charge, and that the slag contained (by assay) 40% of lead. The fire-place had no fire-bars, and the hole in front was kept full of burning brushwood during the *corrida*.

Boliche with coal as fuel.—Three charges of ore of 90 arrobas each, were worked off in about 24 hours, with a consumption of about 46 arrobas of good coal. It was reported that the yield of lead was about 58 arrobas per charge, and that the slag contained (by assay) 40% of lead. The fire-place had fire-bars, and a door was put up in front during the *corrida*: no brushwood was used.

English furnace with coal as fuel.—Three charges of ore, of about 100 arrobas each, were worked off in 24 hours, with a consumption of about 50 arrobas of coal. It was reported that the yield of lead was about 65 arrobas per charge, and that the slag contained (by assay) 25% of lead, which latter statement Dick did not believe to be accurate. There are three stages, as in smelting in the *boliche*, viz.: *caldeo*, lasting from 1 to 1½ hour; *blandeo*, lasting about 5 hours; and *corrida*, lasting the remainder of the shift. Importance was attached to an 8-hours' shift, but Dick says he saw no advantage of such a shift over one of 6-hours.

Much importance seems to be attached to the chamber near the stack and to the bridge which separates it from the working chamber. M. Petitgand designates this bridge as a sort of soul (*âme*) or regulator of the apparatus. The draught of the furnace might be regulated by varying the size of the passages in the bridge, or by a damper in or at the top of the stack; but how that object can in any degree be attained without such an arrangement, or by means of the second accessory chamber, I do not understand, unless air be let into it from

time to time as occasion may require, which, according to Mr. Thomas, is never done.

The two openings in the furnace, namely of the fire-place and that above the lead-pot, are never closed, except temporarily with fuel when it is necessary to moderate the draught.

The bed of the first chamber for about two-thirds of its entire surface is more or less circular, when it loses that form, terminating in a diagonal line, abutting on each side of the working door. In consequence of this arrangement, according to M. Petitgand, the temperature is always higher in the upper part of the furnace; and as the gases cannot be reflected downwards with as much intensity, they do not volatilize the metal which is constantly accumulating in the cavity intended for its reception.

M. Petitgand expresses as follows what he conceives to be the special advantages of the Spanish reverberatory furnace. The interesting feature of this furnace, he says, not only depends on the absence of a grate in the fire-place, which is easily explained by the nature of the fuel used, but also upon the structure of the beds and the construction at their line of junction. [It has been previously stated that modified *boliches* are in use, which are provided with fire-bars and burn coal.] It is proper to fix attention upon these details, of which, so far as he knows, little or nothing has been said, except by Spanish authors, and yet in these artifices resides the whole merit of the apparatus. The gases of combustion hardly formed would escape instantaneously and produce no useful effect, if they were not obliged in some sort to condense in order to attain their maximum intensity. That is what happens here; they undergo a period of check, or rather a kind of continuous eddying action (*remous*) by the constriction of the opening intercalated between the two beds, which forces them to lick (*lécher*) all the internal surface (*parois*) of the furnace in developing their calorific power upon the part which requires, for the reduction of the matters under treatment, a constant and more energetic temperature: in passing over the second bed, the flames, in scattering themselves about, suffer new retardation, which re-acts afresh upon their course and permits the reduced gases to exert their oxidizing action. This second bed regulates the play of the first and tends to maintain the temperature necessary for the re-actions. It has still other advantages, that of aiding to retain the metallic dust and the oxides carried over by the current of air produced by the contraction of the small arch (*i.e.* the arc of intersection between the roofs of the two chambers). These matters can be removed when convenient through the two openings at the angles, as shown in the woodcuts, and through which also air may be admitted when needful to promote the draught. [When the furnace is in full operation air admitted through these openings would check, not promote, draught through the first or working chamber. Excessive draught through the furnace, and consequent lowering of the temperature, might thus be checked, and the temperature thereby increased.] They serve besides for removing matter which may have accu-

mulated in the interior, and might tend to derange the working of the furnace; the smelters therefore are always very careful to keep these parts of the furnace clean and free of obstruction. In all other kinds of reverberatory furnaces, continues Mr. Petitgand, the gases of combustion escape rapidly through the flue connecting the bed with the stack; but the fuel which feeds them has a calorific power and an intensity such as to render it useless to have recourse to the expedient employed in the *boliches*. In reverberatory furnaces most in use the bed is rectangular, octagonal, or elliptical; several doors are made in the sides, either to draw the flame thither or to introduce oxygen from without; but in the Spanish *boliche* so rudimentary, even so rude as one might wish it to be supposed, it has been seen that two openings suffice perfectly for its working, that the gases spread themselves uniformly through it, acquiring in it all their force and action, thanks to the constriction which divides the apparatus. This arrangement exists nowhere else; the Carinthian furnaces (presently to be described) which have in respect to mode of working some points of resemblance, only very imperfectly represent the *boliches*.

Mr. Petitgand, it thus appears, is much impressed both with the ingenuity of construction and the advantage in working of the Spanish furnace. However, I am not convinced by his reasoning of the value of the second or elliptical chamber while the furnace is in operation, so far as concerns the velocity or direction of the gaseous products of combustion in their course to the stack. The action of that chamber, assuming it to be kept perfectly closed, is constant and therefore can have no effect in modifying the draught as occasion may require. There may be and probably is a good ground for it, seeing that it has long experience in its favour, but what that ground is I have yet to learn.

On the other hand it should never be forgotten that although what is called experience may generally be a very safe guide, yet in some cases, especially in the metallurgic arts, it has undoubtedly proved a most erring one and powerfully obstructive to improvement. The practical smelter is not seldom prejudiced, obstinate, and strongly impressed with the notion of his own self-importance. By these remarks let it not be imagined that I specially refer to Spanish lead-smelters, who, I am assured on high authority, understand their business as well as any of their brethren in Great Britain.[5] The opposite evil should also be guarded against, namely, that of pronouncing dogmatically in the absence of, or in opposition to, the teachings of experience, an error which men of science are predisposed to commit.

M. Petitgand states the cost of a *boliche*, completely finished, to be from 390 to 520 francs, or even less (*i.e.* from 15*l.* 12*s.* to 20*l.* 16*s.*), and inclusive of tools and other necessary articles, the total outlay would not exceed 1500 francs (60*l.*).

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[5] Dick informs me that nowhere is the Flintshire furnace seen better at work than at Adra and Berja. The furnaces there in use are larger than those in this country; the charge is also larger, and the work is well done.

The furnaces of Linares and La Carolina are somewhat larger than those used elsewhere, the constricting arch is more open (*l'arceau est plus ouvert*), the first bed is almost entirely circular, and the second is elliptical.

For a charge of 60 arrobas (*i.e.* a little more than 13 cwt.), the quantity stated by Mr. Thomas, inclusive of some rich slag impregnated with metallic lead and of lead-skimmings from previous operations, of which the average produce is from 72% to 75% of lead, between 700 and 800 kilogrammes (1543 and 1764 lbs. avoird.) of fuel are required according to the observations of M. Petitgand.

M. Petitgand presents the following statement of the smelting-costs at furnaces in the vicinity of Almeria :—

For 100 kil. of ore—

Fuel	fr. 1·24	Fr. 2·105.
Labour	0·715	
Iron and miscellaneous	0·15	

Per metrical ton of ore fr. 21·05 = about 16*s.* 10*d.*

For 100 kil. of lead—

Fuel	fr. 2·624	Fr. 4·426.
Labour	1·490	
Iron and miscellaneous	0·312	

Per metrical ton of lead fr. 44·26 = about 1*l.* 15*s.* 5*d.*

The yield of lead was estimated at from 46% to 48%, exclusive of that in the grey-slag (*crasses blanches*), which is extracted by subsequent treatment, and amounts to from 18% to 22%. The lead obtained by this process has a reputation for softness and purity.

According to M. Petitgand, in Andalusia, in the district of Linares, the ores yield by the same method of smelting 50% of lead with the same cost for labour and wear of tools, but per contra greater cost of fuel (*i. e.* fuel composed of shrubs, etc.).

At Alquira, the smelting-costs in the Flintshire furnace there in use are given as follow by M. Petitgand :—

For 100 kil. of ore—

Fuel (English coal)	fr. 1·826	Fr. 2·695.
Labour, etc.	0·869	

Per metrical ton of ore fr. 27 = about 1*l.* 1*s.* 3*d.*

For 100 kil. of lead—

Fuel (English coal)	fr. 3·00	Fr. 4·40.
Labour, etc.	1·40	

Per metrical ton of lead fr. 44 = about 1*l.* 15*s.* 2*d.*

M. Petitgand asserts that the lead produced in the Flintshire furnace in Spain is less pure than that produced in the Spanish *boliche;* and the reason, I am informed, is, that when brushwood is used as fuel there is less reduction of lead from the slag. The difference is, however, too slight to merit attention, though smelters try to obtain a somewhat higher price for *boliche* lead.

It is added by M. Petitgand that the smelters on the coast pretend that they regularly consume $\frac{1}{2}$ ton of coal for 1 ton of lead, but that according to his computation it is $\frac{3}{4}$ ton of coal for 1 ton of lead. It would seem that in regard to economy, the Flintshire furnace has not a decided advantage over the Spanish furnace; but lead-smelting furnaces, like all others, would soon clear a large space grown over with such shrubs as broom, rosemary, juniper, lavender, cistus, etc.,[6] and the cost of fuel, owing to the necessity of fetching it from long distances, must be continually augmenting, and at length might become so great as to render profitable smelting impossible, unless we assume, what is known not to be true, that the growth of those plants is sufficiently rapid to prevent any considerable addition to the cost of fuel on account of the constantly increasing item of carriage. With coal, however, substituted for shrubs, and the seaboard as the site of smelting works, the cost of fuel may be reckoned to be constant, or pretty nearly so; and that assuredly is a decided advantage in an economical point of view, and such points of view are paramount in importance.

After what has been advanced on the subject of the reactions in the Flintshire reverberatory furnace, only a few words need be added as to those which occur in the Spanish furnace. There is first the preliminary calcination with free access of atmospheric air, by which a portion of the charge of galena is changed into sulphate and protoxide of lead; secondly, the usual mutually-reducing action between those oxidized compounds of lead and the unchanged galena consequent on elevation of temperature within the furnace; thirdly, the intermingling and kneading, as it were, of embers, or ignited carbonaceous matter with the residual mass—from which lead has freely liquated and run into the well of the furnace—whereby protoxide of lead may be reduced and sulphate of lead also, partly to sulphide and partly to metal, and then any sulphide so formed would suffer reduction by contact with any remaining protoxide of lead. As the admixture of ignited carbonaceous matter cannot be otherwise than far from intimate in a chemical sense, and as the reduction of sulphate of lead both in kind and degree varies, as we have seen, with the proportion of carbon as well as with the temperature, it is only possible to express in a general way the reducing function of the carbon added in the last or third stage of the process. This carbon, with much intermixed ash, also acts mechanically, like lime in the Flintshire furnace, by "drying" the charge, and so enabling it to be "set-up," with the object previously explained.

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[6] A fresh crop of fuel from these plants may be obtained about every four years. The odour of these Spanish smelting works, where fragrant shrubs are used as fuel, is described as delicious and aromatic, and contrasting remarkably with the "rankest compound of villainous smells" in an English smelting work in which coal is the fuel.

LEAD-SMELTING IN THE FLOWING-FURNACE,

By the Cornish Process.

There are two smelting works, one at Par and the other at Point, on the Truro river, and the process is almost exactly the same at both; and when lead-smelting was carried on at Falmouth, the same process was there also followed. Impure galena is the ore treated (see p. 101). Reduction is effected partly by the reaction between sulphide of lead and the oxidized products of its calcination, and partly by metallic iron and carbon in the form of culm, *i.e.* anthracite. The process consists of two operations termed "calcining" and "flowing" (*i.e.* melting), for which two furnaces are required, one for calcination, the calciner, and the other for fusion, the flowing or melting-furnace.

Calciner.—Calcining-furnaces of two sizes are employed, one suitable for a charge of 2 tons of ore, and the other for a charge of $1\frac{1}{4}$ ton (1 ton = 21 cwts. of 112 lbs.). The last or smaller of these calciners is represented in figs. 70 and 71. In fig. 71, it is shown partly

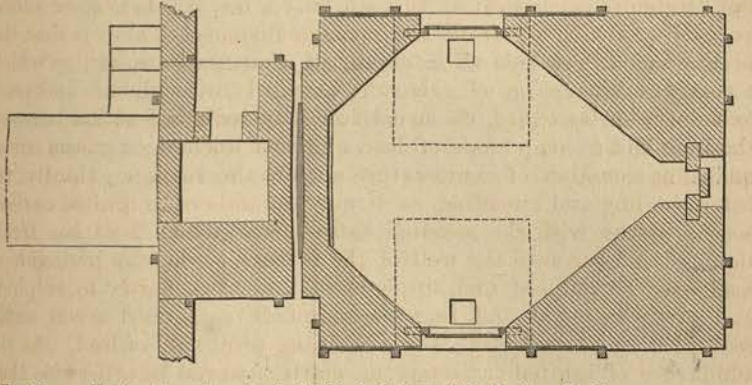

Fig. 70. Horizontal section on a level with the bottom of the fire-door, fig. 71.

in elevation and partly in vertical section on the line bisecting the fire-place and the bed; and in fig. 70, in horizontal section just above the level of the bed. There are three doors, one on each side facing each other, and the third at the end near the stack. There are two square holes in the bed adjacent to the two side doors respectively, through which the calcined ore may be raked into the arched vault underneath, seen in elevation in fig. 71, and in fig. 70 indicated in plan by dotted lines. There is a passage through the fire-bridge from side to side for the free circulation of air, and on the right of this passage is the usual supporting bridge-plate of cast-iron. The furnace is charged through a hole in the roof. The internal lining of the calciner is of fire-brick 9″ in thickness, and the external casing is of common rubble; the sides of the working doors are formed of cast-iron plates or granite blocks.

Flowing or melting-furnace.—Fig. 72 is an elevation of the tap-hole side or front. Fig. 73 is a vertical section on the line C D fig. 74; fig. 75, a vertical cross-section on the line E F fig. 74; and fig. 74, a horizontal section on the line A B fig. 73. As the furnace is only a modification of the Flintshire furnace, which has

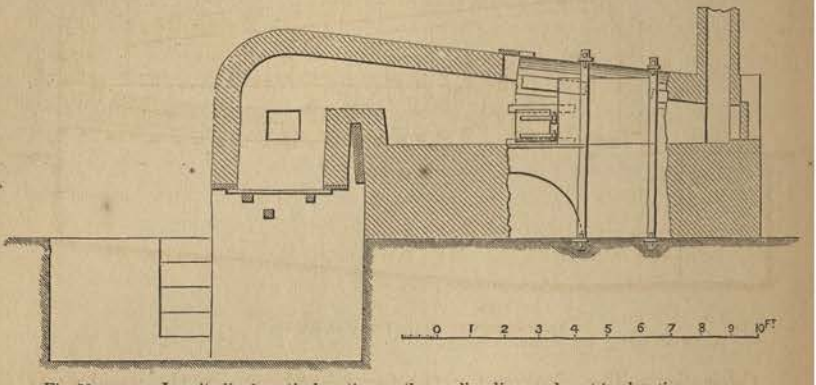

Fig. 71. Longitudinal vertical section on the median line, and part in elevation.

been previously described in detail, all that need be here given in the way of description are the chief points of difference. There are two doors instead of three on each side, *i.e.* in technical language, at the back and front. The bottom is carried on iron bars, which are laid so as roughly to form the contour of the finished bottom. There

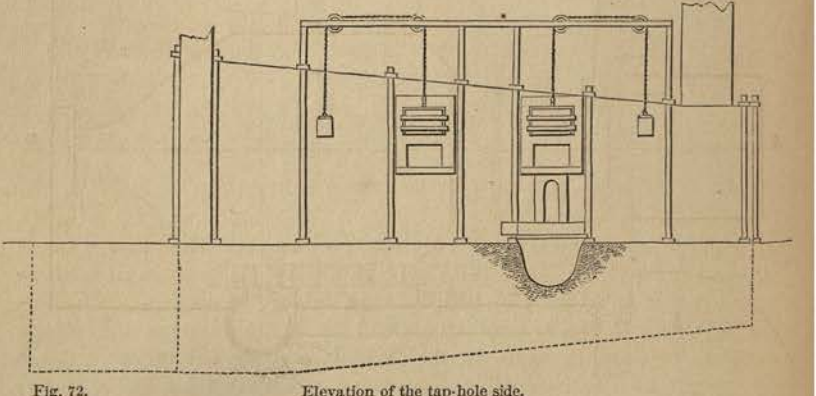

Fig. 72. Elevation of the tap-hole side.

is a little pit, *a*, fig. 74, intended to receive the regulus which overflows the lead-pot by a lip; and outside the smelting-house is a large pit *b*, fig. 74, to receive the slag which flows along a gutter from the lead-pot, the edge of which is surmounted by a ring open only towards that gutter. The furnace is formed internally of a lining of fire-brick 9″ in thickness, and externally of a casing of granite blocks. The upper or true working bottom is made of furnace-slag.

Ore.—Rich and poor ores are mixed together, and the assay produce of lead of the mixture is usually from 65% to 70%. About half of the ore sold is "prill" ore and "sieve beds," yielding by assay an average of 79%.

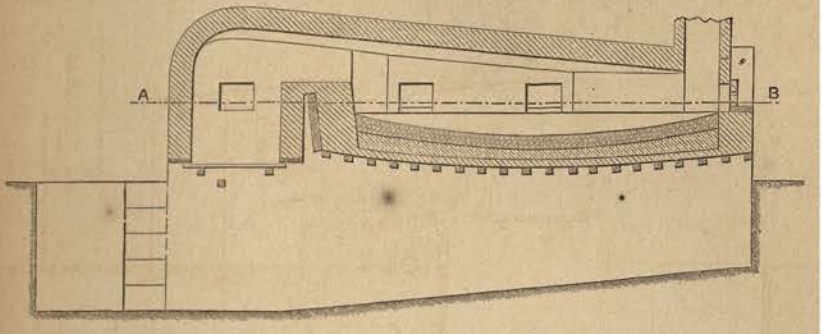

Fig. 73. Vertical section on the line C D, fig. 74.

Calcination.—The charge for the furnace shown in the woodcut is 1¼ statute ton. It is worked by one man, who is served by a labourer with ore, lime, &c. The larger calcining furnace previously referred to is worked by two men, without the assistance of a labourer. The ore is dried on the furnace roof, and dropped through the hole into the

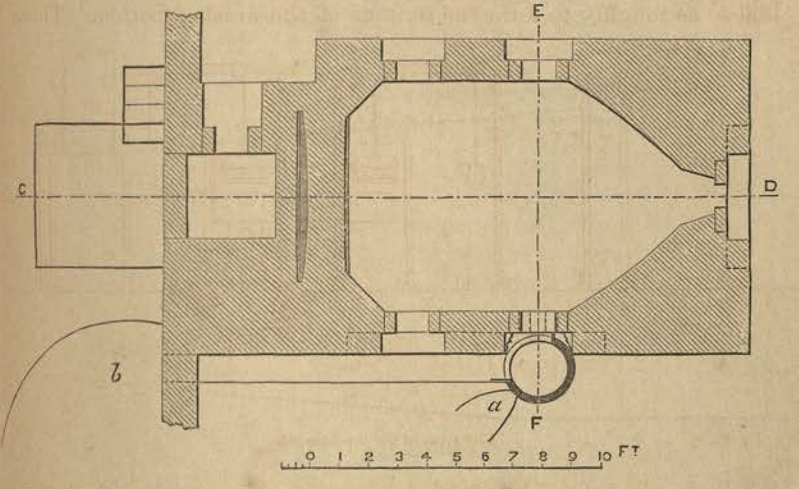

Fig. 74. Horizontal section on the line A B, fig. 73.

interior. Calcination is continued from 15 to 20 hours, and the ore is turned over once an hour, with the occasional addition of lime to prevent clotting. The coal consumed is about 6 cwts. per ton of ore. In many districts the calciner is much larger, and holds a charge of 3 tons.

Flowing or melting.—The charge is 2 tons of calcined ore. It is introduced through the back doors and spread over the sloping bed, which done the doors are luted and the heat raised. It melts in from 2 to 3 hours, and when ores of high produce are being treated, the reduced lead is tapped off at this stage. The molten charge is now mixed with lime and culm, or, as it is termed, "dried up," and then spread over the bed. Fluor-spar is thrown over the charge,[1] and from 1 to 2 cwts. of scrap iron are placed in the furnace at the tap-hole. The doors are again luted and the charge re-melted, after which the furnace is tapped by means of a thin iron bar. Lead flows into the pot, followed by regulus resulting chiefly from the reduction of sulphide of lead by iron in the second fusion. This regulus overflows the pot by a lip into the small pit in front, and on slag beginning to run the tap-hole is much enlarged, and the lip of the pot stopped up with ashes. The slag then runs along the gutter into the pit outside. The whole operation is usually completed in about 8 hours. The flowing-furnace is worked by two men in each shift, with one attendant in the day shift; and it consumes from 8 to 9 cwts. of coal per ton of ore. The slag is generally so "clean" as to admit of being thrown away, and contains only from $\frac{1}{2}$% to 1% of lead by dry assay.

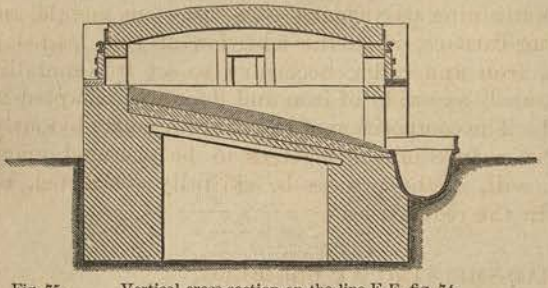

Fig. 75. Vertical cross-section on the line E F, fig. 74.

The greater part of the copper in the ore passes into the regulus, which is calcined and re-smelted in order to extract the lead and silver contained in it, when a second regulus is produced which contains from 8% to 15% of copper, and is sampled for sale to the copper-smelter.

The lead produced is generally so hard as to require softening by calcination at a red-heat, with free access of air,[2] before it is desilverized by Pattinson's process; it contains a little copper, but antimony is the cause of its hardness. The furnace used in the operation of softening is slag-bottomed and similar to the flowing furnace. It is charged with 4 tons of lead, and the softening is commonly completed in about 4 hours.

The plan originally adopted at Falmouth was to smelt the mixture of "prill" and "sieve beds" ore, of 79% produce, alone in the Flintshire furnace, and to mix the slag thus obtained with poor ores, for treatment in the blast-furnace. It was found impossible to smelt the rich Cornish ores with anything like the same facility as those of Wales; and as the produce of a mixture of slag

[1] I am informed that fluor-spar is no longer used at these works (1870).

[2] This process will be described hereafter, p. 458.

and poor ores was from 50% to 55%, it was considered far too high for the treatment of such a mixture in the blast-furnace and too low for advantageous working in the flowing-furnace. The plan was therefore abandoned, and the Cornish one adopted with very satisfactory results so far as smelting was concerned.

I have pleasure in stating, that for the illustrative drawings and the details of the foregoing description, I am indebted to Mr. Thomas Gibb, formerly a student at the Royal School of Mines, and afterwards engaged at lead-smelting works in Cornwall.

The flowing-furnace, as well as the Flintshire furnace, is in use in North Wales and elsewhere, and is known under that name. Its construction and the mode of working it are essentially the same as in Cornwall. It is employed for the treatment of the rich, drawn, grey-slag of the Flintshire furnace, the lead being reduced by iron and culm, with the formation of a clean slag, consisting for the most part of silicate of protoxide of iron and lime, with other bases which may happen to be present, or, in some cases, with fluoride of calcium and sulphate of baryta. Lead residues of various kinds, South-American silver ores, and jewellers' and silversmiths' "sweep," *i.e.* the sweepings of their shops containing particles of those precious metals, are treated in the flowing-furnace, with the addition of rich lead-slag and reducing agents, iron and culm, necessary to set free metallic lead, and with fluxes, such as oxide of iron and fluor-spar, adapted to render the slag liquid. The composition of the charges must obviously vary according to the nature of the matters to be operated upon. The silver and gold will, if the process be skilfully conducted, be wholly concentrated in the reduced lead.

LEAD-SMELTING AT BLEIBERG.

There are some points of interest in this process, as well in respect to the construction of the furnace as the method of treatment. The ore is galena, and reduction is effected by the usual reactions between unchanged sulphide and oxidized compounds of lead generated in a preliminary roasting of that sulphide. The process consists essentially of three stages, which are analogous to those of the Cornish process. For the following description, and the drawings from which the annexed woodcuts have been prepared, I am indebted to Tunner, Director of the Mining School at Leoben, in Styria, whose high reputation as a metallurgist is an ample guarantee for their accuracy.

The galena occurs in Jurassic Limestone: it is accompanied by zinc-blende, which after separation partly by hand and partly by wet dressing, is sold to zinc works; by yellow lead ore or molybdate of lead, which, if present in large quantity, is separated and sold to chemical manufactories for the production of molybdic acid; and by white-lead ore or carbonate of lead, sulphate of lead or anglesite, calamine, and silicate of zinc ($3ZnO,2SiO^3$) or willemite. The vein-stuff is chiefly carbonate of lime: fluor-spar, asbestos, &c., occur also, but seldom. The ore is delivered at the smelting works partly in the

form of coarse ore (Kernschlieg), containing on an average from 66% to 70% of lead, and partly in the form of slime ore (Schlammschlieg), containing from 60% to 70% of lead.

Description of the furnace.—It is reverberatory, and has a bed which slopes regularly from one end to the other, and from each side towards the median line. It is represented in the annexed woodcuts, figs. 76, 77, 78, 79, 80, which have been prepared from drawings of No. 3 furnace in the Spitalerhütte belonging to Sebastian Ebner's Company at Bleiberg, erected in 1859 and still (1868) working well with the same dimensions. Wood is the fuel used in this furnace, except in a few instances.

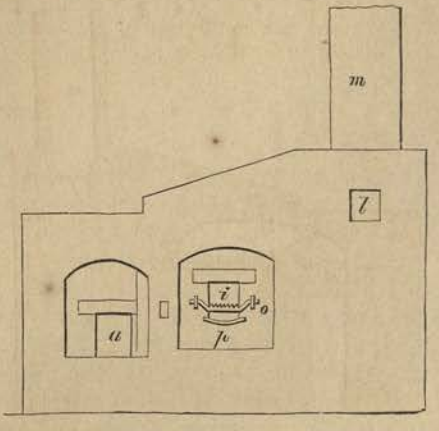

Fig. 76. Front elevation.

The fire-place (*a*) is parallel to the long axis of the bed (*b*). The grate is of stone, and has generally from 4 to 5 transverse openings (*cccc*) each $2\frac{1}{4}''$ wide, for the admission of air: it is 1′ 3″ wide in front, and is contracted to 1′ 2″ at the back. The actual area of this grate is from 122 to 183 square inches. The rise in the whole length of the fire-place is 2′ $6\frac{1}{4}''$. It is only the upper or back part of the fire-place that receives fuel, the lower or front part serving merely as a passage for its introduction.

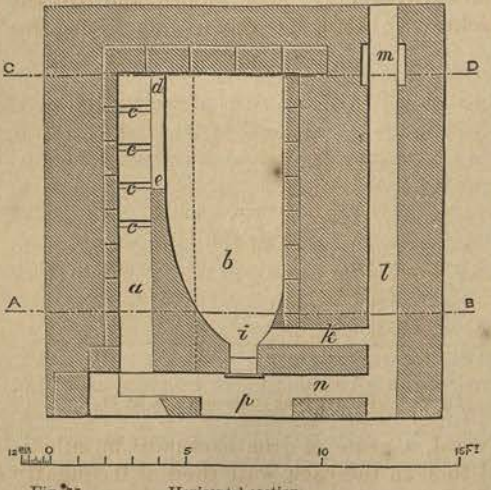

Fig. 77. Horizontal section.

The flame passes from the fire-place into the body of the furnace through a narrow channel (*de*), which, measured according to the rise, is 3′ 6″ long and $6\frac{1}{2}''$ high. The upper surface of the fire-bridge (*f*) is $5\frac{1}{2}''$ broad and 1′ 2″ above the stone grate. The rise in the arch is $9\frac{1}{2}''$, see figs. 78, 79, 81. The working bed, measured according to its rise, is 10′ 4″ long, and from the back end, C D fig. 77, to the front or lower end (*e*) of the flame channel (*d e*) has the same width, which, inclusive of the fire-bridge, amounts to 4′ 10″; but from this end it is narrowed gradually on each side to the working door (*i*), which is 1′

square. The dimensions as to the height of the arch spanning the bed are given in detail in fig. 81. The rise of the bed is generally several inches less than that of the fire-place; and it should be such that the molten lead may easily run down, but not the pasty, earthy constituents of the charge, or any of the sulphide of lead. The bed is gutter-fashioned so that liquid matter must flow to the working door. The flame escapes from the body of the furnace through an opening (*k*), 9″ square, in the crown of the arch, and thence proceeds to the stack (*m*) through the flue (*l*) 1′ wide and 1′ 3″ high. The chimney is 1′ 6″ square, inside measure, and 1′ 9″ high from the flue (*l*): it is generally provided with a damper for the regulation of the draught. In front of the working door is a flue (*n*) communicating with the main flue (*l*), the object of which is to carry off the fume and so protect the workman from its deleterious action. The furnaces are constructed partly of fire-brick, but chiefly of the red sandstone of Bleiberg; the working bottom is 6″ thick, and is usually made of a mixture of clay, poor slimes, and dressed slag (mit aufbereitetem Gekrätze), stamped down and fritted by heating into a coherent mass.

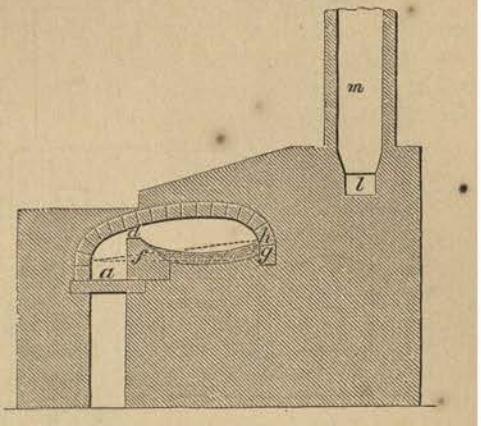

Fig. 78. Vertical section on the line C D, fig. 77.

Modification of the furnace.—At the lead-smelting works at Knappusche in Carniola, the main flue (*l*) is carried entirely round the furnace in order to utilize the heat of the escaping gaseous products of combustion and the prevention as far as possible of the cooling of the body of the furnace. When brown coal is used as fuel instead of wood, a grate of iron bars must be substituted for one of stone; and then in the back-wall there is frequently a small opening for the admission of air. Double furnaces, *i.e.* one over the other, were by reason of their less consumption of fuel, for a long time in use at the Imperial Lead Works at Bleiberg; but on account partly of the frequent repairs which they needed, and partly because they did not admit of the work being carried on in

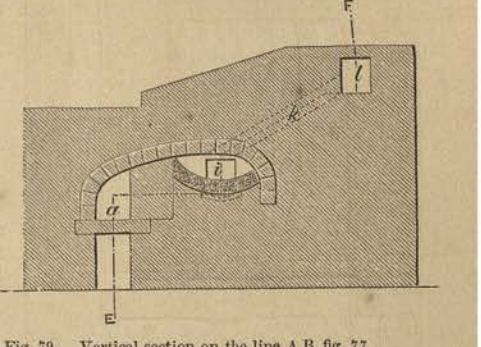

Fig. 79. Vertical section on the line A B, fig. 77.

them with the same precision as in single furnaces, they have been abandoned.

Rivot expresses his surprise at this course, after such a long trial of the double furnaces, and doubts the truth of the reasons alleged for their discontinuance; and he says, that when he was at Bleiberg in 1844, "the double-bedded furnaces were regarded as a very happy improvement."[1] Experience is the great and only test in such matters; and if the anticipations at first formed with respect to the superiority of these furnaces over the single ones had been confirmed by experience, they would unquestionably have continued to be used to this day. It is not the first time that furnaces constructed on a similar principle have failed, as I have shown in the first volume of this work, nor will it be the last. There seems to be no good reason for doubting, as Rivot does, the validity of the causes assigned for the abandonment of the furnaces in question; for not only is there inconvenience in practising the necessary manipulations in such furnaces, but as has been practically demonstrated, considerable expense is necessitated for repairs.

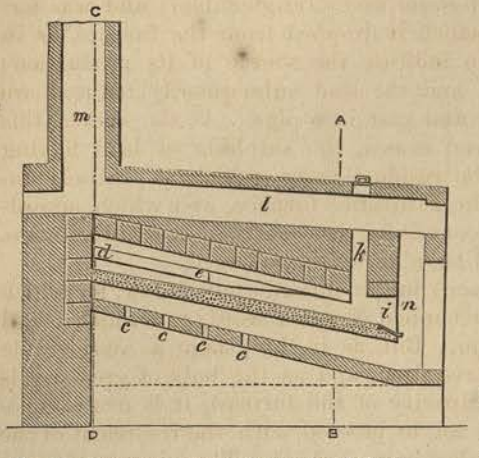

Fig. 80. Longitudinal section on the line E F, fig. 79.

Mode of conducting the process.—After the bottom of the furnace has been prepared and heated to dull redness, a charge of 300 lbs. of ore[2] is shovelled in through the working door (*i*) and spread evenly over the whole of the working bottom, the temperature being kept so low by sufficient admission of air, that roasting may only gradually proceed without the ore becoming soft and adhering to the stirring-rake. The roasting is usually completed in from 3 to 3½ hours, the ore having been raked over 8 or 9 times during that period. Thus ends the *first stage*, which has for its object the partial conversion of the sulphide of lead into oxide and sulphate of lead.

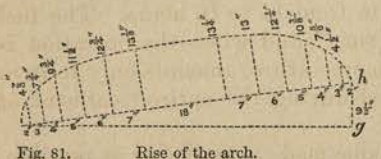

Fig. 81. Rise of the arch.

The temperature is now raised sufficiently to cause the usual reactions between the unchanged sulphide of lead and the oxidized compounds generated in roasting, and the *second stage* (Blei-

[1] Principes Généraux, p. 310.
[2] 100 lbs. Austrian = 123·460 lbs. English avoirdupois.

rühren) or that of rabbling begins, which generally lasts from 3½ to 4 hours. In order to lessen the labour of the workmen, the bar (*o*) is fixed in front of the working door (*i*) as a rest for the heavy tools used in this as well as in the first stage. The rabble is worked assiduously, whereby thorough intermingling of particles of sulphide and oxidized compounds of lead is effected and the resulting metallic lead flows all the while down the inclined bed of the furnace into a cast-iron pot set on the platform (*p*). This lead, by reason, it is alleged, of its great purity, is termed *virgin lead* (Jungfernblei), and was formerly sold in the state in which it dropped from the furnace, *i.e.* in irregular lumps, in order to indicate the source of its production; whereas, at present both it and the lead subsequently reduced are generally liquated together and cast into pigs. At the end of this *second stage*, the flow of lead ceases, the sulphide of lead having entirely disappeared, and the residual mass—which is precisely analogous to the *grey-slag* of the Flintshire furnace, and which, accordingly, I will call *grey-slag*—containing lead only in an oxidized state. From 100 to 130 lbs. of lead have been now collected.

The *third stage* (Bleipressen) might immediately follow, for which there is no corresponding technical English word, and which I will designate *slag-reduction* stage. But, as in this stage a considerable increase of temperature is required, and as the bulk of grey-slag is small compared with the capacity of the furnace, it is more economical with respect to fuel not to proceed with the treatment of the grey-slag until its quantity has been doubled. The mixture of ashes and small charcoal which has dropped from the fire-place is thrown into the furnace and rabbled with the slag, which, thus stiffened, is raked out and provisionally laid aside. Another charge of 300 lbs. of ore is introduced into the furnace and treated exactly like the first, the consumption of time and the yield of lead being the same. At the completion of the second stage, the grey-slag is mixed with small charcoal and that resulting from the preceding charge of ore is put back into the furnace, which now contains the grey-slag produced from 600 lbs. or two charges of ore in from 14 to 16 hours. The fuel burned during this period is very small, and when the operation is carried on at the lowest practicable temperature, amounts only to from ¼ to ⅓ of the total quantity consumed during the entire treatment of those two charges of ore.

The temperature is raised, the flame made as reducing as possible, and small charcoal added when necessary, and thoroughly rabbled with the grey-slag in order to reduce the oxide and sulphate of lead contained in it. This slag-reduction stage requires from 7 to 8 hours, during which period from 120 to 180 lbs. of lead are produced, so that the time needed for completely working off two charges together weighing 600 lbs. is from 21 to 23 hours,[3] the yield of lead amount-

[3] For each charge, roasting, 3–3½ hours; rabbling, 3½–4; total for each charge, 6½–7½. For two charges, therefore, 13–15. Add 7–8 for the slag-reduction of the two charges, and the sum is 21–23.

ing to from 370 to 380 lbs. There are also formed from 90 to 100 lbs. of slag or residue (Gekrätze), containing 3% of lead, which is stamped and washed, whereby a product is got containing from 50% to 60% of lead. This concentrated product is generally added in small portions to a charge in process of smelting; but it is occasionally treated by itself, in which case the first and second stages are omitted.

The lead produced is impure chiefly from mechanical admixture, and as in consequence of its slowly trickling out of the furnace its form is irregular, it is placed at the beginning of a smelting-operation, after the charge has been introduced, upon the foremost end of the bed of the furnace, which is expressly kept free from ore, there liquated, and afterwards cast into pigs.

As a rule there are at each furnace two workmen, of whom each works off two charges of ore, and therefore, remains at the furnace from 21 to 23 hours consecutively: they are paid on the piecework system. An assistant is sometimes engaged at a furnace, who works during a 12-hour shift and has to be supported by the piecework man.

Results of smelting.—At Sebastian Ebner's lead works in Bleiberg, the following results were obtained during 5 weeks, May 1866, in the furnace represented in the annexed woodcuts. These results may be regarded as about the best obtained at Bleiberg.

The following statement is given as received with the local German names of the particular ores smelted in admixture:—

Ores treated.	Ctrs.[4]	lbs.
Weisser Kern (coarse ore), from Kreuth	44	90
Erstollen id. id.	3	50
Vorsichts id. id.	18	0
Erstollen Schmund (slime) id.	45	50
Weisser rascher id. id.	4	0
Zettwerk id. id.	1	0
Hugerthaler id. id.	17	0
Kernschlieg (coarse ore), Bleiberg	85	60
Rascher Schmund (slime) id.	8	22
Bleispatlr Schmund (lead-spar slime) id.	3	28
	231	0

The average content of lead, as found by wet assay, was 67·401%, and after subtraction of tolerated (passbar) loss, 64·08%. The quantity, therefore, of extractable lead amounted to 148 ctrs. 2 lbs. The quantity actually obtained amounted to 149 ctrs. 77 lbs. There was, consequently, produced an excess of lead amounting to 1 ctr. 75 lbs. The consumption of wood in pieces $4\frac{1}{2}'$ long was 10·2 klafters, at 162 cubic feet per klafter, or a total of 1647 cubic feet.

The yield of lead was, consequently, 64·84%, and the actual loss was 2·561% of the *ore*, or 3·79% of the *lead*.

The consumption of wood was 10·9 cubic feet per ctr. of lead extracted, 7·1 per ctr. of ore, or 21·4 ctrs. per charge.

[4] 1 ctr. = 100 lbs. Austrian = 133·460 lbs. English avoirdupois.

In the matter of wages, the workmen have an interest in the result both in regard to consumption of fuel and yield of lead: they are credited with 1·80 florin o. W (*i.e.* "Austrian value," since 1859—1 florin = 100 kreuzers) and per contra debited with 6·40 florins for every klafter of wood which they consume: for every pound of lead in excess of the proper quantity which they extract they receive 0·07 florin, and for every pound less they are mulcted to the same amount: they pay smithery costs. During the month above mentioned there were 35 shifts of 24 hours each, and 77 charges were worked off, for which, consequently, the wages paid were as follow:—

	Florins.
77 charges at 1·80 florin	138·60
Subtract for 10·2 klafters of wood 64·05 florins ..... Id. smithery costs 7·10 id.	71·15
	67·45
Add for 175 lbs. of excess of lead at 0·07 florin	12·25
Net wages	79·70

	Florin.*
The net wages are for each charge	1·03
Id. per ctr. of ore	0·34
Id. per ctr. of lead.....	0·53
The smithery costs are per ctr. of lead	0·047

* Nearly of the same value as the English florin.

Observations.—At the most recent period the weight of a charge has been raised from 300 to 350 lbs. The lead at present produced at Bleiberg, which is known in commerce under the name of "Villacher Blei," has, according to Streng, the following composition:—

COMPOSITION OF BLEIBERG LEAD.

Lead.....	99·9660
Copper	trace.
Iron	0·0039
Zinc	0·0041
Antimony.....	0·0260
	100·0000

This lead without being refined is classed by its producers amongst the purest and softest kinds of lead.

The foregoing description was accompanied by a table of analyses by Ferientsik of the residual products (Reichkrätzen, Armkrätzen, Flammofenkrätzen) of the Bleiberg process, which appears to me to be wholly unsatisfactory; and it is added "other analyses of intermediate products at Bleiberg do not, unhappily, exist."

In confirmation of the opinion which I have expressed concerning Ferientsik's results, I give one of his analyses of rich grey-slag:

ANALYSIS OF GREY-SLAG BY FERIENTSIK.

Lead	69·6
Iron	1·5
Magnesia	6·3
Protoxide of copper	5·5
Sulphur	16·1
	99·0

It is clearly indicated in this analysis that the lead and iron are wholly in combination with sulphur. Now, 69·6 parts of lead require 10·75 of sulphur to form sulphide of lead; and, assuming what is incredible with respect to the iron, namely, that it is present as iron-pyrites, 1·5 part of iron requires 1·71 of sulphur. The total sulphur, therefore, in combination is $10{\cdot}75+1{\cdot}71=12{\cdot}46$. But the total sulphur in the analysis is 16·1. Hence (16·1—12·46 =) 3·64 parts of sulphur were in a free state, and that too in a substance produced at a comparatively high temperature and containing not less than 5·5% of protoxide of copper! Verily it is time that a thorough weeding should take place of the mass of so-called analyses of metallurgical products, which have not only been published, but seemingly accepted, without hesitation in quarters where they ought to have been instantly rejected as worthless.

In 1835 M. Boulanger published the results of an analytical investigation by himself of the products occurring in the Bleiberg process of smelting lead;[5] but as exception may be taken to his method of analysis and to the conclusions at which he arrived, this reference to his labours will suffice.

It is stated that treble furnaces, *i.e.* built one over the other, have been tried at Bleiberg, with a view to carry on the three operations of the process at the same time in the three furnaces respectively; but they were not found to be satisfactory on account of the great inequality in the times required for roasting and the subsequent operations.[6]

The smallness of the charge, only 300 lbs., will strike the British lead-smelter as remarkable. It is insisted that in order to conduct the work with accuracy and precision the charge, and consequently the furnaces, must be small, whereby supervision is facilitated though the consumption of fuel and wages are increased. The temperature should never be allowed to rise so high as to melt the charge, which would in that case run down the inclined bed of the furnace. It is alleged that the low temperature maintained contributes essentially to the purity of the reduced lead, as it is too low to cause separation of other metals; but what, it may be asked, are the metals which

[5] Ann. des Mines, 3rd ser. 1835. 7. p. 167. A description of the double furnace was published by E. M. Phillips, in a paper in the Ann. des Mines, 4th ser. 1845. 8. p. 239, entitled, Mémoire sur le gisement, l'exploitation, la préparation mécanique et le traitement métallurgique des minérais de plomb de Bleiberg en Carinthie.

[6] Phillips, Ann. des Mines, ut supra.

would be reduced at a higher temperature and pass into the lead? If the ores are poor, the temperature is too low for complete reduction and the residual slag is too rich. Lime, if not present in too great quantity, has little influence; and it is often expressly added in order to keep the charge porous. Iron-pyrites and zinc-blende hinder the process and increase the loss of lead from volatilization. Quartz causes the slagging of a large quantity of the oxide of lead formed.

Karsten long ago pronounced the following judgment on the Bleiberg process, which appears to me well founded, and as applicable now as when he wrote. To conduct the process successfully an exact knowledge of the heating power of the furnace and of the degree of fusibility of the ore are required; and that knowledge is readily gained by practice. The fusibility of the ore is affected by the quantity of foreign matter present, and increases in proportion to its purity, so that an impure ore may be treated at a higher temperature than a pure one. As the process requires much time, and is consequently expensive with regard to labour, it can only be profitably adopted in the smelting of rich ores.[7]

According to Rivot "the Carinthian method [*i.e.* the Bleiberg process], is only applicable under special conditions: the ore must be nearly pure, with a gangue of limestone, sulphate of baryta or blende; its content of silver should not be worth consideration, vegetable fuel is almost indispensable, the cost of wood and labour should be very low.[8] . . . It is only possible," he adds, "to apply this method to ores of which the gangues have no tendency to form fusible compounds with oxide of lead. As to the richness of the ore, it ought to be very great, because the *crasses* [the residual slag] are not submitted to any special treatment: it is not permitted to neglect them only because they are produced in very small quantity: with argentiferous ores, the *crasses* would always contain silver, and it would be necessary to treat them in a blast-furnace."

Now, the average content of lead, as determined by wet assay, in the ores treated at the works, from which the foregoing description proceeded, was 67½%; and such ores would certainly not be designated as rich, much less as *very rich*,[9] by British lead-smelters; but it has been customary to smelt in the Bleiberg furnaces ore containing not more than 58% of lead.[1] The impurities which interfere with the process of lead-smelting in the Bleiberg method, would act likewise in the Flintshire, or any other reverberatory furnace, where reduction is effected by the reaction between sulphide and oxidized compounds of lead; so in that respect the Bleiberg method is not singular. It

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[7] System der Metallurgie, 1832. v. p. 103.

[8] Principes Généraux, p. 314.

[9] La richesse du minérai doit être très-grande. Rivot. If much carbonate of lead is present in the ore, it will lose its carbonic acid even before reaching redness; and, consequently, the ore will become relatively richer. Such an ore, though poor with respect to assay-produce, may be virtually regarded as rich by the smelter.

[1] Karsten, System der Metallurgie, 5. p. 101.

might be supposed that vein-stuff, which tends to form compounds with oxide of lead much less fusible than the oxide *per se*, would be more injurious than such as tends simply to form fusible compounds with it; and in aid of that supposition, I refer to the results previously recorded, concerning the reducibility of the different silicates of lead. This objection, which Rivot urges on the ground of fusibility, does not rest on that ground; for the temperature needed to melt those fusible compounds, resulting from combination of the vein-stuff with oxide of lead, would suffice to melt that oxide in a state of isolation. As to the reason assigned for the unsuitableness of the Bleiberg method in the smelting of argentiferous galena, it may be stated, that it is no more inapplicable to the treatment of such ores than any other in which the reverberatory furnace is employed. Suppose the residual slag to contain silver enough to pay the cost of its extraction, and therefore to require further metallurgical treatment, that objection would apply to all other methods of smelting in the reverberatory furnace, in which iron is not in any stage used as a reducing agent; and such a consideration is wholly beside the question of the character of the Bleiberg process strictly so called. But, according to Karsten,[2] the *crasses* or residual slags, which contain from 8% to 9% of lead, were in the usual course stamped and ground; the ground stuff was mixed with carbon and treated alone in a reverberatory furnace; and the lead obtained was termed *Kratzblei*. Moreover, from the foregoing description, it appears that the residual slag from the Bleiberg furnace is not thrown away, but is subjected to special treatment, with a view to extract the lead which it contains.[3]

Lead Assaying at Bleiberg.—As the usual dry assay methods differ too much in their results from each other, during about the last three years the following wet assay method has been practised. Two grammes of the ore as finely powdered as possible are heated with concentrated nitric acid until the residue becomes nearly white, and red vapour ceases to be evolved. A few drops of sulphuric acid are added and the mixture evaporated nearly to dryness. The product when cold is diluted with water, put upon a filter, and washed until the wash-water passes through free from acid reaction. With poor calciferous ores it is better after the treatment with nitric acid not to carry evaporation too far, and before adding sulphuric acid to dilute with $\frac{1}{8}$ of a litre of water. It is also better to use diluted sulphuric acid, as in that case less sulphate of lime precipitates, which can only be separated from the sulphate of lead with great difficulty and by long-continued washing. Upon the filter remain sulphate of lead, silica, some sulphur, and, according to the chemical nature of the ore, sulphate of baryta, some sulphate of lime, and rarely some carbon; while the filtrate contains in solution nitrate or sulphate of lime, magnesia, oxide of zinc, sesquioxide of

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[2] System der Metallurgie, 5. p. 100.

[3] See description of modified Bleiberg furnace by Petitgand, which he used at Davos, in Switzerland. Revue Universelle, vol. ix., 1861, p. 360. A drawing of it is given.

iron, etc. The precipitate is washed off the filter into a beakerglass with a solution of neutral carbonate of soda and digested for an hour with a concentrated solution of that salt. In less time than that, one cannot be certain that the whole of the sulphate of lead has been converted into carbonate of lead, with the formation of sulphate of soda. Sulphate of baryta undergoes no change by this treatment with carbonate of soda. The mixture is filtered and the filter washed with hot water until a drop of the filtrate causes no turbidity in a solution of chloride of barium. The insoluble residue upon the filter is boiled in diluted nitric acid or in acetic acid, filtered, and washed with boiling water until the wash-water ceases to have an acid reaction. The lead is thrown down from the filtrate with the least possible quantity of sulphuric acid, the precipitate is left to subside, and a drop of sulphuric acid is added in order to be certain that the whole of the lead has been precipitated. More sulphuric acid than is actually needed should be avoided with a view to prevent any of the lime present from being thrown down in the state of sulphate. The precipitate of sulphate of lead is filtered, very carefully washed with hot water, dried, heated to redness, weighed, and the proportion of lead computed. If the process is properly performed the assay and counter assay do not differ more than 0·1%, and in many cases less.

LEAD-SMELTING IN PERU.

I am indebted for the following description (1867), from personal observation, to Mr. Ratcliffe, who has been engaged as an assayer in Peru, and had previously studied in the Metallurgical Laboratory of the Royal School of Mines. The locality is the province of Conchucos Altos.

The furnace is represented in figs. 82, 83. It is placed against the side of a sloping bank, and is built of "adobes," or bricks of clay, sun-dried but not burnt. The "plaza" or bed, is made of ashes and clay; the grate is of bricks, and the ash-pit is about 7′ deep, the air being admitted and regulated by the hole at bottom. The dome or roof is made in the form of a triangular arch (if such a term may be used) of adobes, and the interstices filled up with mud and ashes. The chimney is made sloping, and it is said that considerable judgment is required to proportion the height and slope of the flue, in accordance with the kind of ores to be smelted. The fuel used is cord-wood and brush-wood.

The ore was galena, which, assayed by Mr. Ratcliffe, yielded 56% of lead and 444 ozs. of silver per ton. The charge of ore smelted was 243 lbs., Spanish. This ore had undergone no other preparation than that of being crushed to lumps about the size of eggs. It was placed round the edge of the "plaza," as shown in fig. 83, before the dome of the furnace was made; this dome is only temporary, and both it and the bed of the furnace are constructed afresh before every smelting.

The operation was conducted as follows:—the fire was lighted at

3 p.m., and the ore began to melt at 6 p.m.; a strong fire was then kept up till at midnight the bed of the furnace contained a quantity of fluid metal in active ebullition. This temperature was maintained till 4 a.m., when about half of the slag was tapped off by the door, which was afterwards closed with bricks and mud, more fuel being added. At 4·30 a.m. more slag was extracted by means of an iron rod, inserted through the doorway, which was again closed and the furnace left to cool. During the smelting common *salt* was frequently added through a hole left in the top of the furnace for that purpose.

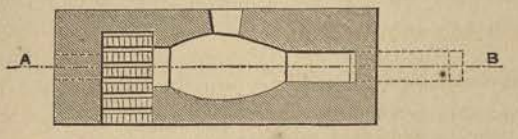

Fig. 82. Horizontal section on the line C D, fig. 83.

When cold, the dome of the furnace was pulled off, and the reduced lead was found in large and small buttons, dispersed through a quantity of litharge-like slag. The bed was broken up, and as much as possible of the lead collected; although a considerable portion was lost, being too finely disseminated through the litharge to allow of its collection. The bed itself was found to be composed of two distinct layers; the upper one had absorbed a large quantity of the slag, and was semi-fused: it contained silver to the amount of 0·289%. The lower layer seemed to be the original bed, only slightly altered by lead-fumes, and contained no silver.

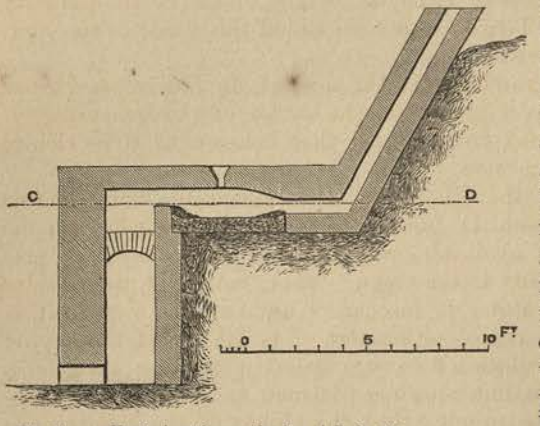

Fig. 83. Vertical section on the line A B, fig. 82.

Of the lead just 6 lbs. Spanish were collected. This was cupelled in a furnace, of the same shape as the first, but much smaller, and having a chimney only about 3′ high. The bed was formed by first placing a layer of wood-ashes, a few inches thick, upon this a layer of thin adobes, and then a bed of bone and wood-ash. This was pressed down first with the hands, then with the feet, and afterwards condensed with a mallet, and smoothed off with a trowel. Upon the bed so formed was placed the lead, on a piece of *sheep's skin*, with the wool uppermost, after which the furnace was then covered in as in the former case. The fire was lighted at 11·30 a.m. and at 3 p.m. the metal melted. A sample was now taken out for assay. A little *soda* wrapped up in paper was placed on the top of the molten metal; the operation was watched through a small hole, and the fire regulated as

necessary. At 5·30 p.m. the action became very intense, and the silver brightened: the fire was now extinguished, and the cake of silver removed with tongs and cooled in water: it weighed 36 ounces Spanish. On breaking out the bed of this furnace, it was found to be very hard and dense, highly impregnated with oxide of lead, and to contain 0·052% of silver.

The results of this smelting were as follow:—

Charge of 243 lbs. of ore, containing	lead	136 lbs.
	silver	48·16 ozs.
Produce of smelting.—6 lbs. of lead, yielding by assay 45·91% of silver, and therefore containing		44 ozs.
Loss of silver in smelting		4·16 ozs. or 8·6%
		48·16 ozs.

Produce of cupellation.—36 ozs. of silver.
Loss of silver in cupelling ..... 8 ozs., or 16·6%

being a total loss of silver of 12·16 ozs., or 25% of the entire quantity contained in the ore. To this must be added the whole of the lead, none of which is recovered.

For effecting this grand result, the smelter, an *Indian*, receives as payment 25% of the silver produced; the owner of the hacienda paying all expenses. It may be imagined that ores ought to be rich to bear such costs for extraction.

There is no doubt that there are *immense* metallic riches in this country, as yet untouched; but nothing at present can be done towards making them available, owing to the impossibility of procuring means of transport to the coast. When, moreover, we consider the existing chronic state of insecurity and uncertainty in this country, owing to the ceaseless ferment of politics, and the supine indifference of the population to any proposal which does not offer a fortune at one venture, but requires patience and time for development, we may cease to wonder that the riches of the country are allowed to remain unproductive. Should its resources ever be opened up by the formation of railways and roads, or perhaps by another race becoming dominant, as seems probable, there is little doubt that Peru will be found to be one of the richest, if not absolutely the richest, country in the world.

Mr. Ratcliffe states that the galena of Peru is often very rich in silver, and as examples of exceptionally rich kinds he mentions the following, which he himself assayed:—

Name of the Mine.	Silver per ton of lead. ozs.
Chuquiral	170
La Virgen	277
La Concepcion	444
La Fortuna	507
La Providencia	1138

The samples of ores assayed were as they came from the mines, and had not been subjected to dressing of any kind. The lead from La Providencia contained ½ oz. of gold per ton.

Unsuccessful attempts at lead-smelting at great elevations in Peru.—I have received the following information concerning unsuccessful attempts to introduce other methods, especially that of the reverberatory furnace. At Mr. Ratcliffe's request I supplied a series of woodcuts of the Flintshire furnace contained in this volume to an English lead-smelter, Mr. H——, who desired to make trial of such a furnace in Peru, and who is reported to have had much experience in lead-smelting in Andalusia. The furnace was accordingly erected, and I have been favoured (December, 1868) with an account of its working from that smelter, which I now present nearly *verbatim*.

"After many difficulties I got my furnace lit, and found that it did not draw well. I built another chimney, lit up again, and then found that with sheep's dung as fuel a longer entrance over the fire-bridge was required. I altered that and set the furnace to work with a charge of 35 arrobas (9 cwts.) of good pure galena; but after the lapse of 2 hours there was no sign of oxidation. I heated 2 hours longer, then raised the heat, etc., and after much labour managed to get a little lead in the basin. I cooled down the furnace and repeated the roasting for 4 hours more, then increased the fire with a view to effect reduction, adding charcoal and lime. I got down a little more lead, and being dissatisfied with the result, I fired hard for 4 hours more and succeeded in melting the whole of the charge. I dried up with lime and drew off about 6 arrobas (1½ cwts.) of lead. The slag, which was abundant, yielded by assay 58% of lead. Believing that I had now an insight into my difficulty, and that want of oxygen was the cause, I charged again with only 20 arrobas (5 cwt.) of galena, so that by using a smaller quantity a larger surface might be exposed to oxidation. The charge remained in the furnace for 24 hours, and I obtained about the same quantity of lead as previously; but in my desperation I had got up an intense fire and found that the furnace had settled. Having been 2 days and 3 nights at the furnace, I was completely used up, and my poor Indians were also worn out; and I threw myself down on my bed in the hope of sleeping, with what feelings you may imagine. After having had some rest, I determined on making further alterations and another trial. I raised the chimney, widened the openings, and lowered the hearth, so as to cause more air to pass through the furnace. The result was better, though still very unsatisfactory; for I only obtained about 30% of lead from pure galena. Thoroughly disgusted with everything and almost ruined, I decided on clearing out, pretty nearly in the same style as poor Dr. —— did: it was in fact but his game over again. I have since ascertained that Richard Spry, at Ayrish, did no better; only he satisfied the people for a time in those days with his small produce, as they knew no better. I am now convinced that it may be regarded as a fact, that it is impossible to smelt lead in a reverberatory furnace at an elevation of 12,000 feet; and I feel certain that even at half that elevation difficulty would be experienced from the same cause. I think that Dr. Percy might make some remarks on this subject, if only to prevent others from wasting capital as too many of us have

done in Peru. I have since learnt in Lima, that the operations of M. Flüker at San Marcos were suspended from a similar cause: they could make copper-regulus, but could neither reduce it, nor smelt lead properly."

Mr. Ratcliffe observes, that "there is a great deal of truth in the idea as to the difficulty in inducing oxidation in these elevated localities. In my own experience in assaying at an elevation of more than 12,000 feet, I found that I could with great difficulty, and with an enormous consumption of fuel—although I had a strong current of hot air passing through the muffle—cupel in 80 or 90 minutes a button of lead, which I could have cupelled at the coast in a third of that time, with much less heat and without any artificial current of air. The want of oxidizing power in the air at these great elevations is, I think, greater than ought to follow from its reduced density. The preceding attempt at lead-smelting in the Andes is not the only one. The Dr. —— above mentioned is an American gentleman, who eight or ten years ago built a reverberatory furnace for smelting galena at Recuay. After much labour and losing all his capital, he experienced the same failure and was forced to beat a hasty retreat. I have seen large quantities of the only product which he could get from his furnace, namely, a dark liver-coloured semi-opaque slag, containing more than 70% of lead, and evidently consisting for the most part of undecomposed sulphides. In one of my journeys through the Andes, I found at Ayrish, a place on the eastern side of the Cordillera and about 13,000 feet above the sea, a large dismantled lead-smelting work almost in ruins. It had been erected, I believe, about 30 years ago, by an American, of the name of Tracy, at great expense, and had been under the management of a Cornishman, named Richard Spry, who had been a smelter at a large work near Saltash. Spry went out to Peru with Trevithick, about 1819, I think, and was for some years employed at Cerro de Pasco. He was still living near Ayrish at the time of my visit. He there erected two large reverberatory furnaces and an English cupellation-furnace at great expense, with all appliances. The iron-work alone cost thousands of dollars, as it had all to be carried from Lima on mules' backs across the snowy range of the Andes, a distance of nearly 200 miles from the coast. He had the advantage of plenty of tolerably good coal at hand; but for all this, the concern came to ruin. At Chonta, which is believed to be the highest permanently inhabited place in Peru, and which is very little under the line of perpetual snow, and where there were formerly very extensive mines of cinnabar, I also discovered the remains of reverberatory furnaces which had been erected for smelting lead and abandoned many years ago. The ore was a ferruginous and antimonial galena. Very little lead was obtained, the product being a dull-looking nearly black slag. The only mode in which I have ever heard of lead ores being smelted with any profit in the Andes, is that with the small native furnaces above described; and here the object is not so much lead-smelting proper as the extraction of the silver existing in the ore. The yield of lead is

very small in proportion to the ore treated, being about from 3% to 5%; but as the silver is more easily reduced than the lead, the yield of the former is proportionally larger, the loss of silver in smelting being only 8% or 10% of that contained in the ore. But this process is only applicable to the small scale, and in places where the supply of wood is abundant."

"Lead-smelting was in operation until a few months back (*i.e.* before March, 1867), at Huari, in the Andes; but as the man, a Mexican, who had the conduct of the work, managed to poison himself with the fumes, the business is now abandoned. He had a small furnace somewhat resembling the *Krummofen* of the Lower Harz, urged by bellows worked by hand. When the furnace 'gobbed up,' he used to stand on the top of it, and poke down the obstruction with a bar, exposed to the fumes of lead all the while. He was seldom free from lead-colic, and at last died of it. He had also a small cupellation-furnace; but as the litharge was never reduced, all the lead was lost, the silver only being obtained."

With regard to Mr. H——'s attempts to smelt galena in the Flintshire furnace in the Andes, the first question that suggests itself is, whether his results should be considered as failures. On this question I have consulted a practical lead-smelter of much experience in this country; and his opinion is that a yield of 30% of lead at the second charge from a new furnace, with perhaps a porous bottom, was very good. The trial ought to have been continued for a month consecutively, under the supervision, say, of two experienced smelters, one attending by day and the other by night, in order to have arrived at a satisfactory conclusion. It is not stated of what material the furnace-bottom was made, nor how it was manipulated; but, in whatever way it may have been prepared, it is certain that it would at first have absorbed a large quantity of lead products. The "settling" of the furnace, which occurred, would seem to indicate either faulty construction or the use of bad materials.

Notwithstanding the alleged want of oxidizing power in the air at high elevations, it is not reported that there was any difficulty in oxidizing even such fuel as sheep's dung; and from the foregoing record of the trials of smelting galena in reverberatory furnaces, it is clear that oxidized products of lead were pretty easily formed; that a temperature was attained more than sufficient to cause the usual reaction between galena and the products of its oxidation; and, therefore, far in excess of what is needed under ordinary conditions of atmospheric pressure to effect the oxidation of galena. At the sea-level it would probably puzzle an experienced Welsh lead-smelter to smelt galena in a Flintshire furnace satisfactorily with dried sheep's dung, instead of good coal, as fuel. It would be interesting to have such a trial made and watch the smelter during its progress.

But Ratcliffe asserts that at great altitudes in the Andes he found assaying by cupellation much prolonged, even to the extent of thrice the time at the sea-level, and that the consumption of fuel was enormous; from which he inferred that the air is deficient in oxidizing

power at such altitudes. It is obvious that the weight of oxygen in a given volume of air in those localities is notably less than at the sea-level; and, consequently, that in the combustion of a given weight, say, of carbon, a correspondingly larger volume of air will be required. The quantity of heat, however, developed on the combustion of carbon by atmospheric oxygen will be the same at high elevations as at the sea-level; but the question arises, whether the energy of combustion and the temperature produced will be practically the same under those considerable variations in atmospheric pressure? To this question may be given a positive answer, founded on the results of experiments made by Tyndall, in August, 1859, at the summit of Mont Blanc. He ascertained that, on burning stearine candles at that altitude, the consumption of stearine in a given time was almost precisely the same as at Chamouni far below, "though the light-giving power of the flame was diminished in an extraordinary degree by the elevation;" and he ascribes this mainly to augmented mobility in the particles of air so rarefied as that at the top of Mont Blanc. He conceives that the particles of oxygen may, by reason of this increased mobility, "penetrate the flame with comparative freedom, thus destroying its light, and making atonement for the smallness of their number by the promptness of their action;" and he finds that, by reducing the density of ordinary atmospheric air to one-half, the mobility of its atoms is nearly doubled.[1]

I am now able to furnish the following additional information on this subject, which I have received from my friend Mr. David Forbes, who has been engaged in smelting arsenical ores of cobalt in reverberatory furnaces at San Baldomero, in Bolivia, at an altitude of 14,400 feet above the sea-level. There was no difficulty, he says, in roasting such ores in open stalls with wood for fuel; but it was found most difficult to produce a melting heat in the reverberatory furnace with wood, which, however, it is added, was of bad quality. At Unduavi, which is believed to be under 11,000 feet above the sea-level, no serious difficulty was experienced in smelting silver lead ores in reverberatory furnaces. At Corocoro and elsewhere, on the high plateau of Bolivia, at altitudes ranging from 11,000 to 13,000 feet, copper ores are smelted without any difficulty in reverberatory furnaces, having two chimneys each, and with only llama-dung for fuel. The step-grate has been applied to these furnaces with great advantage. Mr. Forbes never found any difficulty in cupelling at great altitudes.

After a careful review of the evidence adduced on smelting in reverberatory furnaces at high elevations, and a consideration of the facts established with respect to combustion in rarefied air, I venture to give the following opinion on the subject. It is possible to use the reverberatory furnace for smelting in such localities, even with inferior fuel; but whether it would be possible to do so economically is another question, for the solution of which I do not possess adequate data. However, it will probably be found most convenient as well as

[1] Heat considered as a Mode of Motion, 1865, p. 50.

most economical, under the circumstances, to smelt galena in small blast-furnaces, simple in construction and easily managed; and with this view the ore-hearth, now to be described, in which peat is used in conjunction with coal, should certainly be recommended for trial. But, in order that any such trial should be conclusive, it is essential that the person making it should be practically skilled in smelting by that process. This is a qualification which I hold to be indispensable, unless much time and money be expended in the purchase of the necessary experience.

SMELTING IN THE ORE-HEARTH.

The ore-hearth is a small rectangular blast-furnace or hearth composed of various parts of cast-iron, set in brickwork or other convenient material, which need not be refractory. It is contained within a chamber open in front from the ground to a certain height, and connected above with a flue or other apparatus suitable for the condensation of lead-fume. Such an arrangement is indispensable for protecting the workmen from the injurious action of lead vapour and sulphurous acid which ascend copiously from the hearth; for the prevention of injury to crops and cattle; and for the collection of a large quantity of lead, which otherwise would be wastefully dissipated. Both elements of the sulphide of lead are oxidized by the blast, with the evolution of sulphurous acid; but there immediately follows the well-known reaction between the resulting oxidized product of the lead and the underlying sulphide, whereby metallic lead is separated, so that practically oxidation and reduction may be said to proceed *pari-passu*.

In the early part of the 18th century lead-smelting in Derbyshire was conducted in the ore-hearth exclusively, with charcoal or dried wood, termed white coal, as the fuel, and with the blast of bellows moved by a water-wheel; but when Bishop Watson published his Chemical Essays in 1782, there were not "above one or two of these *ore-hearths* in the whole county of Derby."[1]

The use of the ore-hearth is now confined to the north of England and Scotland. In the United States, my friend, Professor G. J. Brush, informs me, lead-smelting is for the most part conducted in the same kind of ore-hearth as that to be hereafter described. However, at Mineral Point, Wisconsin, reverberatory furnaces are also used. The ore is a very fine galena, associated with magnesian limestone, and is frequently reduced in the ore-hearth in the raw state, *i.e.* without having been calcined.[2]

The accompanying woodcuts, figs. 84, 85, 86, 87, 88, 89, 90, 91, represent an ore-hearth at the Keld Head Mining Company's Smelt-

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[1] V. 3. p. 273.

[2] Most of the lead produced in the United States is in what is called the Upper Mississippi Lead Region, a district of country comprising the northern portion of Illinois, the southern part of Wisconsin, and the eastern portions of Iowa and Missouri.—(*G. J. B.*)

ing Works, Wensleydale, North Yorkshire. The original drawings have been made and supplied by my friend, former student, and assistant, Mr. William Weston; and to the same friend I am indebted for the substance of the following description of the process which he prepared at my request from personal observation.

Description of the ore-hearth.

a. The hearth-bottom or hearth-box, of cast-iron.

b. The work-stone, a flat plate of cast-iron connected with the front edge of the hearth-bottom, from which it slopes downwards; on the sides and lower edge it has a raised border; and from the middle of the upper edge to the middle of the lower edge is a groove, as shown between *b* and *b* fig. 90. Various component parts of the ore-hearth, though made of cast-iron, are termed *stones*. The hearth-bottom and work-stone are cast in one piece; but in ore-hearths

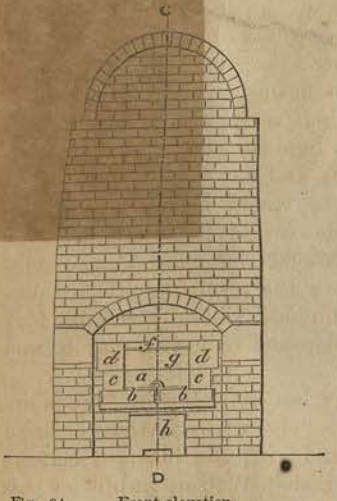


Fig. 84. Front elevation.

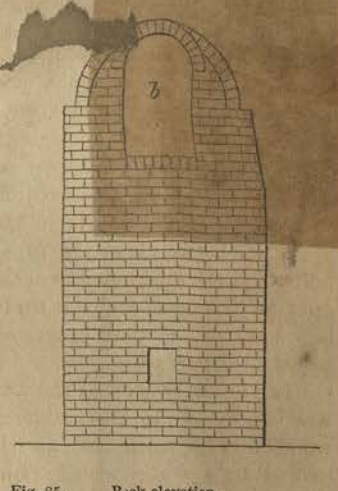


Fig. 85. Back elevation.

in other localities, they are separate castings. The groove is intended to conduct the lead into an iron pot, *h*, in front as it overflows from the hearth-bottom during reduction of the ore.

c, *c*. Two similar rectangular prisms of cast-iron, termed bearers, resting on and somewhat overlapping, the hearth-bottom, one on each side.

d, *d*. Rectangular blocks of cast-iron, termed key-stones, two on each bearer. The two in front are shaped at the back as shown in fig. 91, so as to form ledges for receiving the ends of the fore-stone.

e. The back-stone or pipe-stone.

f. The upper back-stone. These stones, *e* and *f*, form the back of the hearth. Through the lower part of the back-stone, *e*, passes the twyer.

g. The fore-stone of cast-iron, which lies across the hearth, with its ends resting respectively between the key-stones. It can be moved

towards the front or back by changing accordingly the position of the key-stones, or it may be raised by placing fire-bricks underneath it at each end.

Fig. 86. Left side elevation.

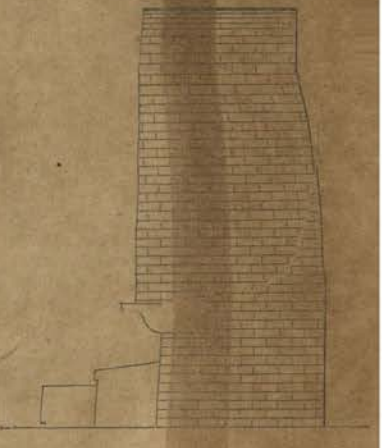


Fig. 87. Right side elevation.

k. The feed-door, through which the workman places a peat before the nozzle and detaches any adherent slag.

w. The flue of the fire-place under the pot. In recently-erected hearths, it has been found better to take this flue direct under the hearth-bottom and curve it to one corner. The space between it and the work-stone should be filled in solid with brickwork.

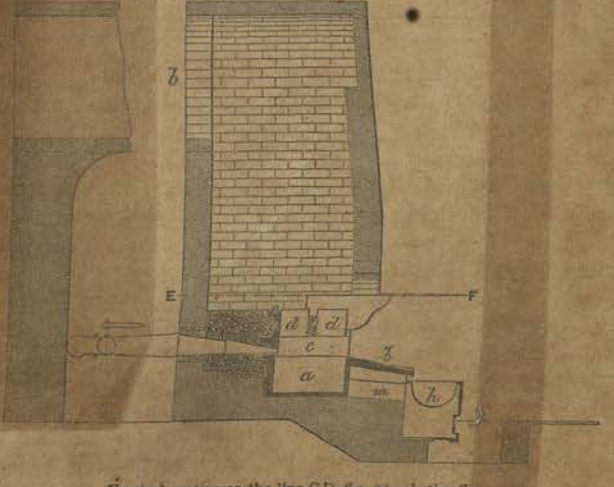


Fig. 88. Vertical section on the line CD, fig. 84. - *b*, the flue.

The dotted space behind the back of the hearth is filled in solid with half-bricks and clay.

The dimensions of the ore-hearth are as follow :—

Hearth-bottom.—1′ 11″ from back to front, 1′ 9″ wide, and 1′ deep, inside measure. The sides and front are 1½″ thick, and the back 2½″.

Work-stone.—3′ 2″ wide and 2′ from front to back. The raised border is 1″ high and the slope forwards and downward is 5″ in its whole length.

Bearers.—2′ long and 7″ square.

Back-stone or pipe-stone.—2′ 6″ broad and 1′ 2″ high.

Upper back-stone.—2′ 8″ long, 5″ wide, and 2″ deep.

Key-stones.—The two at the back are cubes of 10″.

Fore-stone.—Its dimensions may be found in fig. 91 *g*.

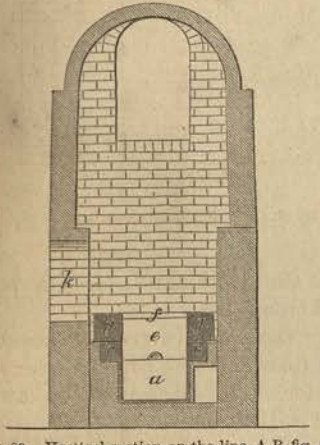


Fig. 89. Vertical section on the line A B, fig. 86.

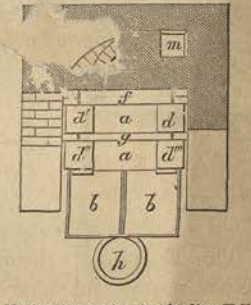


Fig. 90. Horizontal section on the line E F, fig 88.

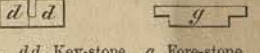
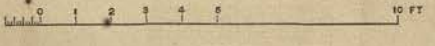


Fig. 91. *d d*. Key-stone. *g*. Fore-stone.



Mode of conducting the process of smelting.—Two men are required, and a shift lasts 8 hours. The fuel is coal and peat cut in prismatic pieces from 9″ to 12″ long by 2½″ square. Such a piece of peat is called *a* peat, and the plural, peats, is used. Lead ore is termed *bouse* in the North of England, and the agglomerated masses of ore formed in the process of smelting are termed *brouse* or *browse*. The ore at the Keld Head Company's Works is *not* previously calcined. The blast is varied considerably according to the nature of the ore operated upon.

The hearth is supposed to be in working order, and the bottom left nearly full of lead, after the last shift. A small quantity of coal is laid on the hearth-bottom, and the remaining cavity of the hearth is filled with peats, which are well walled up in front, while smaller pieces are thrown in without order behind. A few ignited peats are next placed before the nozzle, and the blast is let on. As soon as all the peats are well ignited, a little more coal is added, and shortly afterwards

a little of the brouse from the last shift is thrown on behind the fore-stone. When about half of the brouse is worked in, lead begins to flow; and then one of the workmen stirs up the contents of the hearth with a poker, throwing them forward away from the blast, a portion falling on the work-stone. At this moment the other workman introduces his scraper through the feed-door and removes any slag from before the blast, throwing in front of the nozzle a peat, which disperses the blast and keeps open the fire. Both men then step to the front with their brouse-shovels, and put back into the hearth what had fallen on the work-stone, setting up the contents so that the blast shall be well distributed throughout. Lead now flows freely. Ore in small quantities is added where the fire seems hottest. The stirring up of the contents of the hearth is repeated at intervals of about 5 minutes where the fire is seen to burn badly on account of imperfect diffusion of the blast. At each stirring a fresh peat is placed in front of the nozzle; and from the portions, which during this manipulation fall upon the work-stone, lumps of *grey-slag* are picked out and laid aside for subsequent treatment in the slag-hearth. The pieces of brouse are broken up and returned to the hearth, after which fresh ore is added. When the receiving-pot is full of lead, the latter is skimmed and laded into pig-moulds. During a shift these operations of stirring, lading, etc., are performed alternately by the two workmen. Thus, the man who has been using the poker, lades out the metal, while the other skims it; and the latter attends at the feed-door while the former uses the poker.

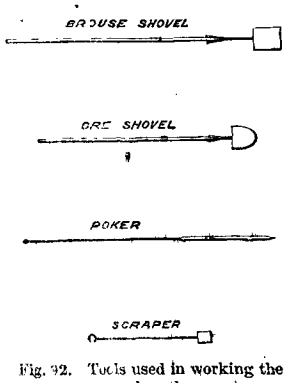


Fig. 92. Tools used in working the ore-hearth.

Towards the end of the shift no more ore is charged; but the contents of the hearth are afterwards worked up two or three times, after which the blast is stopped. All the brouse is taken out, thrown on one side, and separated from the intermingled grey-slag. Lead is laded from the receiving-pot back into the hearth-bottom, so as to fill it ready for the next shift.

Composition of the Slag.

The slag is a heterogeneous mixture, and contains particles of carbon and metallic lead irregularly diffused. It has been examined in my laboratory by Ward. It was triturated and sifted, whereby 8% of lead was separated, which contained 0·6% of sulphur. After this treatment the slag was found to contain 34·12% of lime (existing partly as fluoride of calcium), 9·28% of sulphate of baryta, magnesia, oxide of zinc, alumina, oxide of iron, silica, and 23·74% of lead, existing chiefly as protoxide, but partly as sulphide and sulphate. The total sulphur amounted to 2·44%.

RESULTS OBTAINED FROM ONE WEEK'S SMELTING OF THE SAME ORE AT THE KELD HEAD MINING COMPANY'S WORKS.

Number of shift.	Weight of ore used.	Produced.				Weight of brouse at beginning of first shift.	Weight of brouse at close of last shift.	Percentage of lead *direct* from the ore.	Fuel consumed.			Cost of peat.
		Lead.		Grey-slag.					Coal.	Average cost of coal for each shift.	Peats.	
	cwts.	cwts. qrs. lbs.		cwts. qrs. lbs.		cwts.	cwts. qrs. lbs.		cwts. qrs. lbs.	*s. d.*	Bushels.	*s. d.*
1	32	24 0 0		1 2 18		3	..	..	1 0 5	..	4	..
2	32	24 0 0		2 0 18		..	..	..	1 0 5	..	4	..
3	32	24 0 0		2 0 6		..	..	..	1 1 0	..	4	..
4	32	24 0 0		2 2 0		..	..	..	1 1 8	..	4	..
5	32	24 0 0		2 1 0		..	..	..	1 0 5	..	4	1 5 per ton of lead
6	32	22 3 18		2 0 0		..	3 0 3	..	1 0 5	0 8¼	4	
	192	142 3 18		12 2 14		..	..	74·44	6 3 0	4 1½	24	10 2

The diminution of produce of lead at the last shift is due to the abstraction of the quantity necessary to be put back into the hearth-bottom to fill it up to its overflowing point, at which it was arranged it should be at the beginning and end of the trials. Accurate information concerning the quantity of fume produced could not be procured.

Comparative results from the smelting of the same kind of galena as that which yielded the results in the foregoing table in the reverberatory furnace, and in the ore-hearth.—These results have been communicated to me by Mr. W. Weston, and were obtained at the Greenside Mines in Westmoreland, before the railway was made to Penrith, when the price of coal in that town ranged from 14*s.* to 17*s.* per ton. The coal had to be carted a distance of 17 miles to the smelting works, by which the price was raised to 21*s.* 4*d.* per ton. The present price of coal at Keld Head is 13*s.* 9*d.* (March, 1868).

REVERBERATORY FURNACE.

The quantity of ore worked was 36 tons, which yielded 24 tons 13 cwts. 0 qrs. 17 lbs. of lead.

	£	*s.*	*d.*
Coal, 27 tons 18 cwts. at 21*s.* 4*d.* per ton	29	15	2
Six smelters at 20*s.* per week each	6	0	0
Three roasters at 20*s.* per week each	3	0	0
Three labourers at 15*s.* per week each	2	5	0
	£41	0	2

ORE-HEARTH.

The quantity of ore worked was 12 tons, which yielded 8 tons 3 cwts. 2 qrs. 8 lbs. of lead.

	£.	*s.*	*d.*
Coal, 2 tons 12 cwts. 2 qrs. 0 lbs. at 21s. 4*d.* per ton	2	16	0
Roasting 12 tons of ore at 1*s.* 11¾*d.* per ton.....	1	3	3
Smelting 8 tons 3 cwts. 2 qrs. 8 lbs. of lead at 9*s.* per ton	4	0	0½
	7	19	3½

Cost of smelting 36 tons of ore in the reverberatory furnace ...					41	0	2
Do. do. ore-hearth					23	17	10½
					17	2	3½
Yield of lead from 36 tons of ore in the reverberatory furnace	tons. 24	cwts. 13	qrs. 0	lbs. 17			
Do. do. in ore-hearth	24	10	2	24			
	0	2	1	21, at 20*s.* per cwt....	2	8	9
					£14	13	6½[3]

These results are interesting up to a certain point. They were, doubtless, made with a definite object, which is not stated. That they do not present a fair comparison between the two systems of smelting will be evident to any one who has given attention to the subject, and who knows the position of the two works and their relative

[3] This is exclusive of the cost of bricks.

proximities to peat and coal. To compare the systems fairly, we must assume that the peat and coal necessary for the Ore-Hearth, and the coal necessary for the Reverberatory Furnace, can be supplied with equal facility, and that both are managed with the utmost economy of labour. In a former part of this volume we have seen that 36 tons of ore (the quantity operated upon) would form about 34 charges, each of which would require the labour of two smelters for 5 or 6 hours, and a consumption of from 11 to 13 cwts. of coal of moderate quality, costing, say, 9 shillings per ton. The cost, therefore, would not exceed 15*l.* (instead of 41*l.* 0*s.* 2*d.*); and I am assured by a practical authority that 34 charges of Keld Head ore could be smelted for that sum; but it would neither include the cost of reducing slags, which would be small on so trifling a quantity of ore, nor many other expenses, such as management, general maintenance, wear-and-tear, &c., for which a further considerable sum would be needed. These expenses do not seem to have been taken into account in the foregoing comparison under either system; and in so far the comparison holds good. The wear-and-tear in ore-hearths is certainly less than in reverberatory furnaces; but probably insufficient to cover the considerable balance against ore-hearths, so that we may expect to see the former displace the latter in all but a few localities where coal cannot be got at a moderate price.

Variations in the Construction and Dimensions of the Ore-Hearth.

Mr. Pattinson published an admirable description of the ore-hearth and the mode of working it, from which the following particulars are extracted.[4] The woodcut on the following page has been prepared from the engravings accompanying Mr. Pattinson's description. It is a vertical section from front to back on the median line. The hearth is composed of twelve pieces of cast-iron.

g. Hearth-bottom, 22″ square, inside measure; the bottom 3″ thick; and the sides 3″ thick and 4½″ deep: it is open in front. Between the hearth-bottom and the brick or stone bed on which it rests, is usually interposed a layer of sand a few inches thick. The work-stone is shown sloping 3″ or 4″ from the front edge of the hearth-bottom: it is 3′ long, 1½″ broad, and 2½″ thick, having a raised border 1″ high on its two sides and in front, with a channel 2″ wide and 1″ deep running diagonally across it. The space between the under surface of the work-stone and the brick or stone bed is generally filled up with fire-clay, or with a mixture of slime-ore and bone-ashes duly tempered with water.

b. Bearer, a square prism 6″ on the side and 26″ or 28″ long:

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[4] An Account of the Method of Smelting Lead Ore and Refining Lead, practised in the Mining Districts of Northumberland, Cumberland, and Durham, in the year 1831, by Mr. H. L. Pattinson. Trans. of the Nat. Hist. Soc. of Northumberland Durham, and Newcastle-upon-Tyne, v. 2. part 1. p. 152. In my opinion this is one of the best metallurgical descriptions in the English language.

there is one on each side. They overhang somewhat the sides of the hearth-bottom, and so tend to keep it firm in its place. There is an advantage in making them long, as they can then be turned when worn at one end.

a. Back-stone, a prism 28″ long, 6½″ high, and 5″ broad. The bellows-pipe rests upon this stone.

f. Pipe-stone, a prism 10″ square, and 28″ long, with an opening on the under side to receive the bellows-pipe.

e. Upper back-stone, a prism 28″ long, 4″ high, and 5″ wide, which completes the back of the hearth.

d. Fore-stone, a prism 26″ long, 6½″ high, and 5″ broad.

c, *c*. Key-stones, exact cubes 10″ on the side. There are two on each side. The two nearest the back are placed upon the bearers, *b*, so as to be level with them on the inside, and they are therefore 22″ apart; but the two in front are made to lie against the ends of the fore-stone, *d*, and they are therefore 26″ apart.

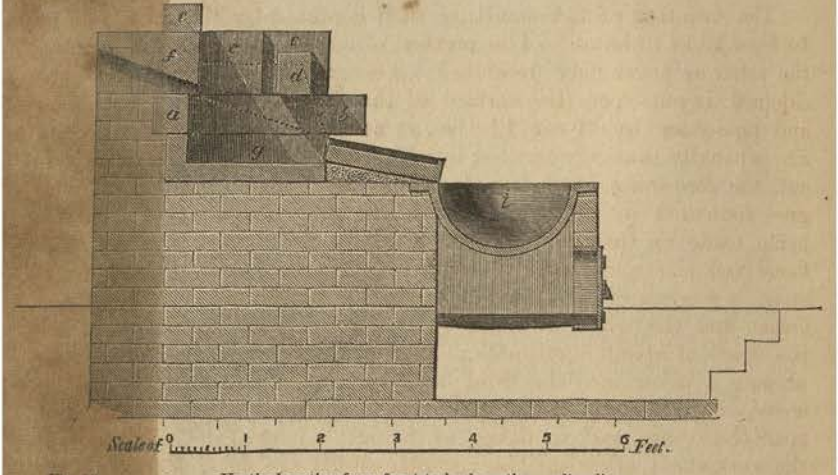


Fig. 93. Vertical section from front to back on the median line.

i. Pot of cast-iron to receive the lead as it trickles down the channel in the work-stone.

The fore-stone is moveable to a certain extent. It can be placed 10″ from the back-stone, by being put in contact with the two key-stones nearest the back; and, if necessary, it can be raised by the insertion of a fire-brick at each end between it and the bearer: its usual position is 11″ or 12″ above the upper edge of the work-stone. The various parts of the hearth are secured in their places by brick-work; and at the top it is finished level with masonry to receive any particles of ore, called *hearth-ends*, which may be expelled by the blast or projected by decrepitation. Each hearth is placed under a chimney, as in the woodcuts of the Keld Head Mining Company's ore-hearth.

The bellows-pipe is shown entering the hearth 6½″ above the level

of the upper edge of the work-stone; but more generally, on account of a little sinking of the bearers and hearth-bottom posteriorly, it is not more than 3″ or 4″ above the surface of the lead. The blast, according to Mr. Pattinson, is always directed downwards to the upper edge of the work-stone, as indicated by the lower dotted line (fig. 93). "Another modification of the hearth adopted by some intelligent smelters (such as has been previously described), is making the bottom, instead of 4½″, 10″ or 12″ deep, by this means increasing the quantity of lead retained in the hearth, and proportionally *lessening its tendency to get too hot*, during the process of smelting." The italics are mine. A very obvious plan of keeping down the temperature of the hearth-bottom, would be to make its sides hollow and blow air through, or an iron pipe might traverse it, through which cold water should circulate. The simple expedient of cooling it by the circulation of air round the exterior has been adopted at certain lead works, and is regarded as an improvement too novel and important to be divulged for the benefit of lead-smelters in general!

The duration of the smelting shift is stated by Mr. Pattinson to be from 12 to 15 hours. The method of commencing a shift is much the same as previously described. The ore having been previously calcined, is put upon the surface of the fire between the fore-stone and pipe-stone by 10 or 12 lbs. at a time. The contour of the fire is usually that represented by the upper dotted line in the wood-cut, the fore-stone, *d*, being drawn forward and raised to the degree indicated by placing a fire-brick underneath it. "The fire being made up into shape represented by the dotted line, with the flame and blast principally issuing between the fore-stone and work-stone, a stratum of ore is spread upon the horizontal surface of the *brouse*, and the whole suffered to remain exposed to the blast for the space of about 5 minutes. At the end of that time, one man plunges a poker into the fluid lead, in the hearth-bottom below the *brouse*, and raises the whole up, at different places, so as to loosen and open the *brouse*, and in doing so, to pull a part of it forwards upon the work-stone, allowing the recently-added ore to sink down into the body of the hearth. The poker is now exchanged for a shovel, with a head 6″ square, with which the *brouse* is examined upon the work-stone, and any lumps that may have been too much fused are broken to pieces; those which are so far agglutinated by the heat as to be quite hard, and are further known by their brightness, the grey-slags, being picked out and thrown aside to be afterwards smelted in the slag-hearth. A little slaked lime, in powder, is then spread upon the *brouse*, which has been drawn forward upon the work-stone, if it exhibit a pasty appearance; and a portion of coal is added to the hearth, if necessary, which the workman knows by experience. In the mean time, his fellow workman, or *shoulder-fellow*, clears the opening, through which the blast passes into the hearth, with a shovel, and places a peat immediately above it, which he holds in its proper situation, until it is fixed, by the return of all the *brouse*, from the work-stone into the hearth." The fire is made up again into the

shape before described, and the same manipulations are repeated. "At every stirring a fresh peat is put above the nozzle of the bellows, which divides the blast, and causes it to be distributed all over the hearth; and as it burns away into light ashes, an opening is left for the blast to issue freely into the body of the *brouse*. The soft and porous nature of dried peat moss, renders it very suitable for this purpose; but, in some instances, where a deficiency of peats has occurred, blocks of wood of the same size have been used with little disadvantage."

Mr. Pattinson states that the principal particulars to be attended to are the following:[5]—1. The blast should be carefully regulated. If too weak the ore is not reduced, and if too strong the contents of the hearth are melted. Both these evils should be avoided; but no special rules can be given, as the same blast is not equally suitable for every kind of ore. In no case should the blast be more than sufficient to reduce the ore. 2. The blast should be as much divided as possible and made to pass through every part of the *brouse*. 3. The hearth should be vigorously stirred at intervals, and a portion of its contents exposed upon the work-stone, when the partially-melted lumps should be well broken to pieces and the grey-slag picked out. This breaking to pieces, and exposure of the hotter part of the *brouse* upon the work-stone to the oxidizing action of the atmosphere, has, according to Mr. Pattinson, a most beneficial effect in promoting the reduction of lead; and lead always flows most abundantly out of the hearth, immediately on the return of the *brouse*, after that treatment. 4. The quantity of lime used should not exceed what is needed to thicken the *brouse* to the proper degree, "as it does not, in the least, contribute to reduce the ore by any chemical effect: its use is merely to render the *brouse* less pasty, if from the heat being too great, or from the nature of the ore, it has a disposition to become very soft." 5. Coal should be supplied judiciously.

When the ore is readily smeltable, and the hearth is skilfully managed, there is formed but a small quantity of *brouse*, which feels dry when stirred, and the contents of the hearth are easily kept open and permeable to the blast. Reduction proceeds quickly with a moderate degree of heat, and the slag produced is inconsiderable. All the so-called earthy matter in the ore impedes the smelting process, and increases the quantity of slag. A very slight difference of composition in perfectly dressed ore affects its reducibility; and hence ore from different veins, or from the same vein in different strata, is frequently found to work very differently when smelted singly in the ore-hearth. With the best workmen, therefore, some varieties of ore require more coal and lime, and a higher temperature, than others; and for this reason the fore-stone is made moveable, so as to answer for ore which works with a large or a small quantity of *brouse*.

At the end of a shift of from 12 to 15 hours, the hearth, in spite

[5] I have, as far as I considered desirable, used the precise words of Mr. Pattinson.

of every precaution, is apt to become too hot, and must be left to cool for some time. In the case of 12-hour shifts, smelting is usually suspended 5 hours after each shift. From 4½ to 5 bings (36 to 40 cwts., 1 bing = 8 cwts. avoirdupois) of ore are smelted during a shift, yielding from 9 to 10 fodders (1 fodder = 21 cwts. of 112 lbs. to the cwt.) of lead, and the two men who manage the hearth work four shifts a week each. At almost every smelting work a different mode of working, with respect to time and quantity, is pursued. In some cases the quantity of ore smelted in one hearth, in a week, by four men, is 40 bings; but a fair rate of working is from 30 to 35 bings a week.

With ore of moderate goodness, 6 cwts. (avoirdupois) of coal suffice to smelt from 18 to 20 bings of ore; but with refractory ore much more is required. The coal consumed is usually at the rate of from 1½ to 2 cwts. per fodder of lead; the quantity of peats used in the same time is about four small cart-loads, or somewhat less than a cart-load per fodder of lead; and the quantity of lime is somewhat below 3 bushels per fodder of lead.

It may be asked why should the contents of the ore-hearth be kept floating on melted lead? The answer is that if the bottom were formed of brick or other solid refractory material, inconvenience might be caused by corrosion or the accretion of slaggy matter, whereby the level would be changed and the working of the furnace deranged. A bottom of iron would be rapidly acted upon. Let the reader try to suggest a substitute for the simple and usual hearth-box filled with molten lead, and he will probably be puzzled.

Treatment of Hearth-ends.

The hearth-ends produced in smelting in the ore-hearth consist of particles of ore, projected from the hearth partly by the action of the blast, but chiefly by decrepitation of the ore, and of particles of fuel and lime. They are collected from time to time, washed in order to free them from non-metalliferous matter, roasted at a strong heat until they soften and cohere into lumps, and in this state smelted in the ore-hearth precisely in the same manner as the original ore. The hearth-ends obtained in smelting 9751 bings of ore, yielded by this treatment 315 cwts. of common lead; and the grey-slags from the same quantity of ore yielded by reduction in the slag-hearth to be subsequently described 47 cwts. of slag-lead, the lead from these two sources being at the rate of 3 cwts. 2 qrs. 23 lbs. per 100 bings of ore. The slag-lead extracted from the fume, collected in smelting the same quantity of ore, amounted to 500 cwts., being at the rate of 5 cwts. 0 qrs. 14 lbs. of lead per 100 bings of ore.[6]

American Ore-Hearth.[7]

It was first introduced at Rossie in the State of New York, wood

[6] Pattinson, op. cit. p. 165.

[7] The following description is founded on that in the American Journal of Science and Arts, 1842, p. 169. The annexed woodcut is also copied from that in the same volume.

being the fuel. I am informed by my friend, Professor G. J. Brush, that the lead mines in that locality have ceased to be worked long ago, and the furnaces have consequently been abandoned.

Description of the hearth.—It is represented in figs. 94, 95. A. The hearth-bottom or hearth-box of cast-iron, 24″ square, 12″ deep, and

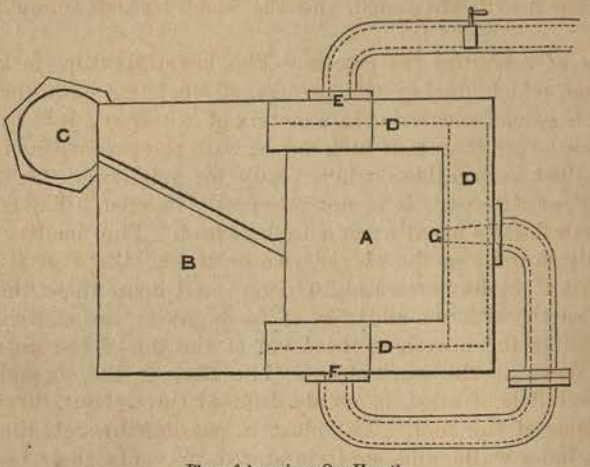


Fig. 94. Plan of American Ore-Hearth.

2″ thick. B. The work-stone of cast-iron, 32″ wide and 22″ from front to back: it has raised borders at the edges or flanges, slopes downwards about 1″ in 12″, and has a diagonal groove on its upper surface for the flow of lead from the hearth-bottom into the cast-

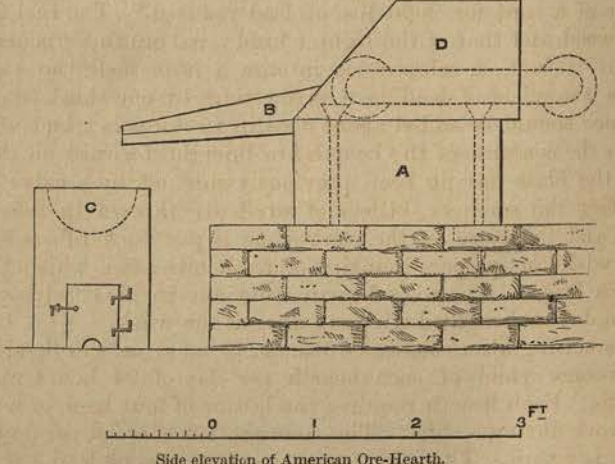


Fig. 95. Side elevation of American Ore-Hearth.

iron pot C, which is set over a small fire-place. D is an air-chest of cast-iron, 14″ high, which forms a wall on the sides and back of the hearth; it is 6″ wide, outside measure, and the thickness of the

cast-iron is about $\frac{3}{4}$", so that inside is a vacant space of $12\frac{1}{2}$" by $4\frac{1}{2}$." The blast passes into this chest through a pipe at E and out at F, whence, by a curved pipe, it is discharged into the fire through a twyer cast in the air-chest at D, 2" above the level of the top of the hearth-bottom. By this arrangement the sides and back of the hearth are cooled, and the blast heated before it reaches the fire.

Mode of conducting the process.—The hearth-bottom is kept filled with lead, which, during the process of smelting, continues molten. The ore is galena, occurring in a matrix of calc-spar; it is broken into pieces not larger than half-inch cubes, with the production of as little fine ore-dust as possible: when ready for smelting it retains from 5% to 10% of calc-spar: it is not previously roasted. The contents of the hearth float as usual upon a bath of lead. The smelter puts immediately in front of the twyer, two or three billets of light wood, say, about 2" in diameter and 16" long; and upon these the contents of the hearth, with the addition of fresh galena, are thrown up, thus nearly filling the hearth to the level of the top of the air-chest and sloping down to the work-stone. The blast is let on, and, striking upon the billets of wood, is evenly diffused throughout, carrying with it the flame of the fuel. The blast in passing through the air-chest cools its inner-walls, and so, it is stated, prevents their becoming so hot as to be quickly destroyed by the sulphur of the ore; and the hearth is thereby kept at a moderate and uniform temperature; whereas otherwise the temperature would soon rise so high as to melt the galena and check the smelting. Moreover, as the blast becomes heated in its course through the air-chest, there is, it is alleged, great economy of fuel, the quantity of wood consumed being less than a quarter of a cord for 2000 lbs. of lead reduced.[8] The fuel is exclusively wood, and that of the lighter kind: coal or other "concentrated fuel," it is said, developes too intense a heat near the blast, and reduces the yield of lead in a given time by one-third or one-half. Fresh ore should be added about once in 10 minutes; and when this is done the contents of the hearth are brought forward on the work-stone, the blast having been previously shut off by a valve in order to protect the smelters, billets of wood are thrown in front of the twyer, and the mass on the work-stone is put back into the hearth along with the proper quantity of fresh ore, after which the blast is again let on. These ore-hearths continue in blast without intermission day and night during six days of the week.

In smelting about 5,000,000 lbs. (2232 tons) at the Rossie Works, the average yield of each hearth per day of 24 hours was about 7500 lbs. Each hearth requires the labour of four men, of whom two only work during a shift. The consumption of wood per day in each hearth is $\frac{3}{4}$ cord. The cost of smelting 7500 lbs. of lead, exclusive of

[8] A cord = 128 cubic feet, $\frac{1}{4}$ cord = 32 c. f. Deduct $\frac{1}{3}$ for interstitial space, which leaves, say, 22 c. f. Put the weight of 1 c. f. of light wood = 35 lbs. Hence, 1 lb. of wood was consumed for 2·6 lbs. of lead.

interest on plant, of superintendence, of producing blast, etc., is as follows :—

Two smelters at $1·50 per day each	$3·00
Two assistants at $1·0 do.	2·00
¾ cord of prepared wood at $2·00 do.	1·50
	$6·50
Or, per ton of lead, about	1·75 or 7s. English.

Results of smelting in the American ore-hearth at Bleiberg in Carinthia.— An experimental ore-hearth on the American principle was in operation at Bleiberg in 1849 ; and was specially erected in consequence of the high and increasing cost of fuel, with a view to ascertain whether, with respect to fuel, this process was more economical than the other well-known method of smelting in that locality, and if so to what extent. The following are the results obtained in the years 1849, 1850, and 1851 :—

Year.	Average per-centage of lead in the ore.	Loss of lead per cent., exclusive of lead in the slag, etc., of which much would be recovered.	Wood consumed.	
			For 1 centner of ore. Cubic feet.	For 1 centner of lead. Cubic feet.
1849	71·52	10·42	3·24	5·08
1850	71·70	9·74	3·14	4·86
1851	70·27	11·38	3·65	5·83

1 Vienna centner = 100 Vienna lbs. = 123·46 English lbs. avoirdupois.
1 do. cubic foot = 1·075 English cubic foot.
The item wood includes that corresponding to the charcoal which was used.

The following observations by Plattner were published subsequently to the paper from which the preceding results have been extracted.

In the American hearth at Bleiberg 25 ctrs. of mixed raw ore, containing on the average from 70% to 71% of lead (by dry assay), were smelted in 12 hours, yielding from 61% to 62% of pure lead, and some slag pretty rich in lead. Of the larger and purer ore (Kernschlich), containing on an average of from 72% to 75% of lead (by dry assay), from 30 to 32 ctrs. were smelted in 12 hours, yielding from 63% to 64% of lead, exclusive of what was in the slag. In the preparation of assay-lead, the purest ore, containing 74% of lead (by dry assay), was smelted to the amount of 45 ctrs. in 12 hours, with a yield of from 66% to 67% of lead, and the formation of some rich slag. The consumption of billet-wood, inclusive of some charcoal, was from 3½ to 4½ cubic feet per centner of lead reduced. The slag (Gekrätz) was analysed by Plattner, who assigned to it the following composition.[9]

[9] Berg. u. hüttenm. Zeit. 1854, p. 22. | Ueber das Verschmelzen des Bleiglanzes | in einem nordamericanischen Schmelzofen zu Bleiberg in Kärnthen.

COMPOSITION OF SLAG.

Silica	5·260
Sulphuric acid	5·038
Protoxide of lead	37·710
Sesquioxide of iron	19·500
Oxide of zinc	19·200
Molybdic acid	0·460
Lime	8·856
Magnesia and protoxide of manganese	1·417
Alumina, with traces of potash, soda, and protoxide of copper	1·760
	99·201

Results of smelting in the American ore-hearth at Przibram in Bohemia.—These results were published by Köller in 1856.[10] The air-chest is made in parts, each having a twyer, $2\frac{3}{4}$″ wide and 2″ high. The hearth-bottom is of cast-iron, $1\frac{3}{4}$″ thick, 24″ from front to back, 20″ wide, and 10″ deep. The work-stone is of cast-iron, $\frac{3}{4}$″ thick, 25″ from front to back, and 34″ wide. The shift lasts 12 hours, during which five men are employed, who work in alternation, so that two work at a time with a third who supplies ore and fuel. The ore is added by 5 and 12 lbs. at a time, according to circumstances. The pressure of the blast is equal to a column of water of from 15″ to 22″ high. In 24 hours from 60 to 74 centners of ore are smelted, with a consumption of 50·1 cubic feet of wood-charcoal and 53·4 cubic feet of wood. The ore contained 74·88 lbs. of lead per centner (*i.e.* 74·88%) and an average per centner of 16 loths 1 quint of silver. The direct yield was 60·68% of lead, *i.e.* exclusive of what would be subsequently extracted from the slag. This slag amounted to 45·94% of the ore.

LEAD-SMELTING IN INDIA IN SMALL BLAST-FURNACES.

The process of lead-smelting as conducted by the natives of India is, as might be anticipated, simple, primitive, and on a very small scale, representing the infancy of the art. The ore is galena and the furnace is urged by bellows. The following description is founded upon information published by Captain Dixon, of the Bengal Artillery, in 1831.[1] The mines occur at elevations from 100 to 350 feet in a range of hills in the vicinity of the city of Ajmír, which is 220 miles S. W. of Delhi, and 230 W. of Agra. It was inferred that these mines had been worked during many centuries. The excavation in following a vein of ore is only made large enough to admit a man moving on his hands. Shafts, galleries, and adits, if not quite unknown, are altogether neglected. The ore is found in a continuous vein averaging from 3″ to 6″ in thickness, the bearing being gene-

[10] Oesterreichische Zeitschrift für Berg- und Hüttenwesen, 1856, p. 341.

[1] Some account of the Lead Mines of Ajmír (Ajmeer). Gleanings in Science, No. 28, April, 1831, p. 111. Calcutta. I have adhered, as far as practicable, to the language of the author.

rally N.E., or, rather, between N.E. and E. It is easily traced from the innumerable shining particles of which it is composed. Sometimes, it is black, porous or spongy; and at others deep red; but the prevailing colour is yellow or ochreous. This variation in colour is ascribed to the nature of the soil in which the ore is imbedded. The author mentions also the occurrence of ore in beautiful crystals imbedded in quartz, called by the natives *surma*, and sold, as taken from the mines, as antimony; and, it is added, "lumps of this ore, weighing from 2 to 3 lbs. have been used as antimony, for laboratory purposes, in the Ajmír magazine, in their natural state." The author was evidently no mineralogist; but it is clear that the substance to which he here refers is galena, though it may be very puzzling to explain how galena should have served as a substitute for sulphide of antimony in the Ajmír magazine. The strata traversed by the veins are described as "sandstone, free and slaty; chalk (?) and quartz rock." Immediately afterwards the author defines chalk as a greasy saponaceous earth, sometimes beautifully streaked, at others perfectly white, and of little density."[2]

There is no blasting with gunpowder, and the hard quartz ore rock is excavated by the old method of *fire-setting*, which consists of lighting a fire of wood against the working face, whereby the rock is cracked to a certain depth and fragments of it are split off.

The mining tools are few and simple in construction. They consist of two or three hammers of different weights, of iron chisels or wedges edged with steel, and of a few one-handed picks. The miners begin work about sunrise, and enter the mine stark naked, each man carrying a small lamp in one hand. The ore is broken as it is gotten into small pieces, for convenience of carriage, and put into small bamboo baskets. As the gallery is not high enough to allow the miners to stand upright, they sit on their haunches in a row and pass the baskets on from one to another. When the whole has reached the foremost man, they move upwards and again seat themselves in a row; and this is repeated until the mouth of the mine is reached.

Mining is chiefly carried on by persons to whom it has descended hereditarily from time immemorial. The miners being very limited in their means were formerly obliged to resort to money-lenders in order to get the funds needful to enable them to carry on their operations; but the interest was most exorbitant, and absorbed most of their profits. But, when Captain Dixon visited the mines, advances were made without interest by the government, and "the miners were wholly emancipated from the rapacious grasp of the money-lenders;" and "the result," says the author, "has fully justified the expedient." The government as lord of the manor received a share of the metal and purchased the balance "at an assigned and rather favourable price." The annual produce was about 850 cwts. of lead.

The ore is spread out on the hill, levelled for a few square yards

[2] The editor of the "Gleanings" very properly questions the statement respecting chalk, and suggests that the author most likely confounded it with *potstone*.

at the entrance of the mine, and there left, if wet, until it becomes quite dry. It is then beaten with cylindrical bars of wood, from 3″ to 4″ in diameter, and about 2½′ long, one end being thinned and curved for convenience of grasping. Holding the handle with both hands, the workmen continue to beat the ore until the whole of the metallic particles have been separated from the matrix, which is collected from time to time and thrown down the face of the hill. After complete pulverization, which is effected much sooner than would be imagined from the rude manner of execution, and after separation of the matrix, the ore is put into baskets and subjected to levigation in water. In the absence of running streams pits from 10′ to 12′ square, and 3′ to 4′ deep are made, and filled with water by bullock power as is usual in irrigating land. Each ore-washer has a wooden tub shaped like the frustrum of a cone, 3′ in diameter at the top and 1′ at the bottom, and 1′ 6″ deep. The ore-washer places himself on the edge of the pit and floats his tub containing pounded ore and water. The contents of the tub are "violently stirred up with the hands," while the tub, owing to its shape, is kept floating all the time. After this stirring, the tub is gradually drawn backwards and forwards on the surface of the water, when the heavier or metalliferous particles subside quickly to the bottom, leaving the specifically lighter sand and other impurities at the top, which are easily skimmed off by hand. This operation is repeated 20 or 30 times until the ore is completely cleansed. The sediment, which accumulates in the pits, is from time to time removed, and the water in the pits is renewed once a week, or oftener, when evaporation is considerable. The washed ore is delivered to a separate set of people, who mix it intimately with its own weight of fresh cow-dung and roll the mixture into balls of about the size of a pigeon's egg, which are left exposed to the sun until perfectly dry.

The furnace is nearly cylindrical, 11″ in diameter at the top and 10″ at the bottom, and 5′ high. Three somewhat angular clay pipes or nozzles are luted to the circumference (*i.e.* I presume, at or near the bottom on the same level, and one at each third of the circumference), and serve to convey the blast from as many bellows, made of half-dressed goat-skin, each bellows requiring the labour of one man. In each nozzle a hole is left for cleansing the end or stirring up the ignited ore, as also for enabling the smelters to observe the interior of the furnace. At the bottom is a tap-hole, and on the opposite side 5″ higher is a hole for the outflow of slag. The author states that the three bellows are worked simultaneously, and "the blast is so disposed as to fall in the centre of the base;" but the bellows were doubtless worked in alternation, so as to produce an unintermitting blast. Charcoal is the fuel, of which ½ to ⅔ of the yield of lead is required. After first lighting the furnace, which is fed alternately with balls and charcoal, tapping takes place in about 3 or 4 hours, the slag being drawn off before the lead, which runs into moulds. The subsequent tappings when the furnace is in full working condition recur about every 1½ hour. The quantity of lead smelted in such a furnace in

one day of about 9 hours, averages from 2 to 3 cwts. The lowest yield is about 31% of lead, the average 40%, and the highest from 50% to 58%.

It is evident that Captain Dixon was neither a mineralogist, geologist, miner, nor metallurgist; for otherwise his description would have differed much from what he has communicated. This is another illustration of the difficulty, not to say impossibility, of describing from personal observation a simple metallurgical process with necessary detail and accuracy in the absence of previous special education on the part of the observer. In this Indian process, the galena would quickly melt and accumulate at the bottom of the furnace, where it would be exposed to the three oxidizing jets of atmospheric air, and so be desulphurized, but not without much loss of lead by volatilization.

ROASTING AND DEOXIDIZING PROCESS.

LEAD-SMELTING AT SALA IN SWEDEN.

For the following description I am indebted to P. M. Sewén (Berghauptmann), the manager of the Sala Smelting Works.

In the mines of Sala, silver occurs but rarely either in the native state or in combination with other metallic elements, as with antimony in the form of antimonial silver, or with mercury as native amalgam; although the latter is said to have been found there about two hundred years ago.[1] Usually the silver occurs in a sulphuretted condition associated with sulphide of lead in the form of argentiferous galena. This mineral is sometimes tolerably pure, and occurs crystallized either in cubes or in rhombic dodecahedra. When not crystallized its structure may be granular, foliated, or finely micaceous; or the ore may be extremely fine-grained, and break with (*skyggmalm*) a steel-like fracture. The argentiferous galena is commonly associated to a greater or less extent with other metallic sulphides, such as zinc-blende, iron-pyrites, magnetic pyrites, geokronite, boulangerite, and more rarely with antimony-glance, mispickel, &c.

These ores occur in irregular veins (*Gångar*) coursing through granular limestone (*Urkalk*), and are more or less intermingled with the minerals of which the vein-stone consists, such as carbonate of lime, chlorite, and talc, salite, epidote, and actinolite. They are also associated with layers of hälleflinta (composed of about $\frac{2}{3}$ orthoclase and $\frac{1}{3}$ of quartz), and with serpentine: occasionally quartz, heavy spar, and other minerals are present. As the ore-deposits are not separated by well-defined walls from the enclosing rocks, the ores are disseminated through the surrounding limestone, or, as it were, infiltrated into its fissures, to a distance of several fathoms from the main mass, sometimes on one side, sometimes on the other, and occasionally on both sides of the vein. As the disseminated ore decreases in quantity in passing from the principal deposit, the ground at

[1] Native amalgam was found at Sala in the years 1660, 1689, and 1696. Act. lit. Suec. 1720, p. 59.

length becomes too poor for working, and finally passes into a pure white or greyish-blue limestone entirely destitute of ore.[2]

In consequence of the manner in which the ore is thus associated with the vein-stuff, it is necessary to explain the mechanical treatment by which it is prepared for smelting. The dressing consists of the following operations, viz.:—

1. *Handskrädning* (breaking by hand).—The ore is broken by hand into pieces of the size of the fist, and is freed from much of its adhering vein-stuff; but with the poorer ores this operation requires great care, practice and judgment. The cobbed ore is divided into two sorts:—

(*a*) *Stuff*, or the rich ore which, being free from vein-stuff, may be smelted without further treatment.

(*b*) *Wask* or stamp-ore.—This is the poorer ore more or less inter mixed with vein-stuff, and must be concentrated to slimes by stamping and washing. In this way most of the ore is treated.

2. *Trättning* or *Sköljning* (washing).—This operation is applied to the fine-powdered ore produced during breaking, and the small mine ore—the so-called *Grufsyltan* or *Grubenklein* of the Germans. These ores are separated by washing into "stuff" and "wask."

By these two operations (breaking and washing) there are produced two qualities of ore—the stuff and the wask. The former is divided into two kinds according to the proportion of metal present, viz., *Helstuff*, or "whole stuff," containing on the average 0·279% of silver and 34% of lead; and *Halfstuff*, or "half stuff," containing 0·132% of silver and 14% of lead. The "wask" has an average yield of 0·0168% of silver. These proportions are cited as an example from the year 1866, but they vary somewhat from year to year. The stuff-ore goes direct to the lead-smelting furnace, but the wask-ore requires to be first concentrated by stamping and washing.

3. *Bokning och Waskning* (stamping and washing).—The poorer ores, or those associated with much vein-stuff—the so-called "Wasken"—are reduced by these operations to the condition of slimes, in order to be smelted with the stuff-ores. The crushing is performed by ordinary stamps working on a cast-iron bed laid on a stone floor. The stamped ore is assorted into three qualities, viz.:—*Grofmjöl* (coarse meal), *Finmjöl* (fine meal), and *Slamm* (slime). The last-mentioned product is further assorted into several degrees of fineness, of which the "toughest" cannot be advantageously concentrated and is therefore at once transferred to the raw-smelting or ore-furnace, while the other sorts are subjected to the further operation of washing (*Waskning*). This process is performed on the shaking-table (*Stosshärd*), and yields the following products, viz.:—

---

[2] The old mine of Sala is remarkable as having been wrought to the great depth of 165 fathoms, almost entirely without the use of gunpowder; the primitive method of fire-setting being still continued, *i.e.* breaking down the rock by making a fire of wood against the working face. In consequence the excavations are very large and irregular, but stand well, and the travelling is done upon staircases instead of ladders.

Grofmjöls slig (coarse slime), with an average content of 0·205% of silver, and 23·1% of lead.
Finmjöls slig (fine slime), with 0·22% of silver, and 28·6% of lead.
Slamm slig (mud-slime), with 0·252% of silver, and 31·2% of lead.

These varieties of slime are smelted with the stuff-ore, in the lead-smelting furnace.

The smelting process at Sala resolves itself, properly speaking, into two distinct operations, viz., *Råsmältning*, or raw-smelting, and *Förblyningssmältning*, or smelting for lead.

1. Räsmältning (*Raw-smelting*).

In this process the charge consists partly of the "toughest" slimes from the stamps mentioned above, and partly of the *Aftrar*, or the finely-divided ore which settles in the further portions of the launders during the washing, and which contains sufficient galena to repay the cost of smelting. These ores, forming the charge in the raw-smelting, pass under the name of *Rågods* (raw goods). With these ores there is introduced an admixture of raw iron-pyrites, quartz, and broken slag from the lead-smelting process, together with the impure slag formed immediately before tapping, and the furnace-residua from the cleaning of both the raw- and the lead-smelting furnaces, since these retain a portion of the regulus, and therefore hold more or less silver and lead.

Calculation, verified by experience, shows that these substances are mixed in each charge in the following proportions:—

	Swedish centners.
Raw stuff (rågods)	0·60
Raw iron-pyrites	0·60
Quartz	0·30
Furnace products from the raw- and lead-smeltings	1·20
Slag from lead-smelting	0·80
Total charge	3·50 centners.[3]

From the raw stuff, which contains on the average 0·0299% of silver, there is obtained by this first smelting process a regulus (*Skärsten*) containing sulphide of lead and silver, and having an average content of 0·114% of silver, part of which is derived from the residues introduced from the lead-smelting.

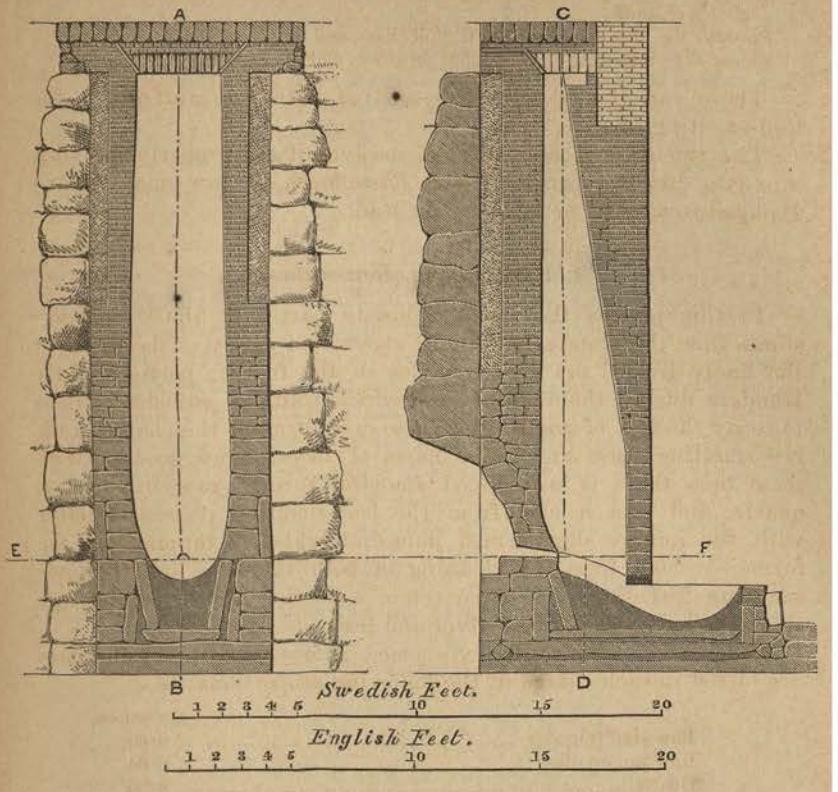
The fuel employed in both the smelting operations, is charcoal made from either the pine (*Pinus sylvestris*) or the fir (*Abies excelsa*). The slag from the raw-smelting consists of a basic silicate of protoxide of iron, and is of no value whatever.

The raw-smelting is conducted in a blast-furnace (*Högugn* or *Schachtugn*), furnished with one twyer (*Öga*) and a fore-hearth (*Framsump*). This furnace is similar in construction to the lead-smelting furnace in the accompanying woodcut, but is somewhat larger.

[3] 1 centner Swedish = 0·837 cwt. of 112 lbs. avoird., *i.e.* 24 centners = about 1 ton English.

Fig. 96. Vertical section on the line C D, fig. 97.

Fig. 97. Vertical section on the line A B, fig. 96.



II. Förblynings- or so-called Bly-smältning (*Lead-smelting*).

This, which is the most important of the metallurgical operations at Sala, is conducted in two blast-furnaces, which are represented in the annexed woodcuts, figs. 96, 97, 98. It is not considered necessary to give a detailed description of the construction of furnaces of this kind, as such descriptions will be found elsewhere in this work. The hearth is made of brasque, and is prolonged outwards and forwards, thus forming a fore-hearth. The charge is composed of "stuff-ore," or the richest ore from the first crushing, and of slimes (*Sliger*) from the washing-process; together with the regulus called "Skärsten" obtained from the first smelting, and that derived as a by-product during the second smelting; the *Skärsten* having been first calcined in

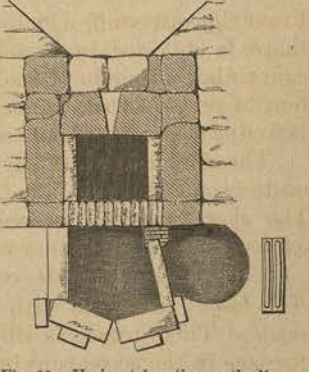


Fig. 98. Horizontal section on the line E F. figs. 96, 97.

an open kiln. Formerly the ores also were subjected to a previous calcination, but as this has been found to entail an unnecessary expense and to be attended by loss of metal, the ores are now smelted in a raw state. It is from these substances—stuff, slime, and regulus—that the argentiferous lead obtained in this process, is derived; other ingredients being introduced partly to produce a good fusible slag, and partly to assist in freeing the metals from their combination with sulphur, or as it was formerly termed, to "precipitate" the lead. For the first purpose, namely the formation of a slag (the proportion of which must bear a proper relation to the production of metal and regulus), there is added some easily-fusible slag containing less lime and more protoxide of iron as bases—such a slag as that obtained from the lead-smelting. The chief points are—that it flow easily, and that it contain sufficient protoxide of iron: hence it should be composed of singulo-silicates (*i.e.* tribasic) because the presence of a greater proportion of silica in the slag increases the loss both of the silver and the lead. To assist in reducing the lead from its sulphuretted condition, metallic iron was formerly employed; but it has been found that the use of it may be dispensed with, by introducing a proper admixture of iron-pyrites, in addition to the "Skärsten," or regulus, from the lead- and the raw-smelting; both the pyrites and the *Skärsten* having been previously calcined. The amount of protoxide of iron which these contain appears to be sufficient to assist the reduction, and to induce the formation of a good slag.

These substances are charged in the following proportions:—

	Parts.
Stuff-ore, containing on an average from 0·13% to 0·28% of silver, and 14% to 34% of lead	100
Slimes from the washing, containing on an average from 0·2% to 0·25% of silver, and from 23% to 31% of lead	125
Roasted regulus (Skärsten) containing about 0·125% of silver	96
Roasted iron-pyrites	18
Slag from previous lead-smelting	750

In addition to the substances mentioned above, there are introduced, during this process, the following lead-bearing products derived from the cupelling-furnace, viz.:—

Abstrich (Abzug?) or the scum which is removed from the surface of the melted lead previously to its oxidation, and which contains a quantity of metallic lead together with any impurities which may have been mechanically mixed with the "work-lead."

Härd (hearth), the bed of the cupelling-furnace which, as it contains a notable quantity of silver in addition to lead, should be treated in the process of lead-smelting.

Glete (litharge). This is added as occasion may require. The litharge used is generally that which is produced either at the commencement [on account of its containing entangled Abstrich?] or at the termination of cupellation, since this contains the greatest proportion of silver.

These argentiferous products are added during the lead-smelting

in order properly to adjust the proportion of silver in the ore-furnace lead produced; for if the lead be too highly argentiferous, a greater proportion of silver remains in the regulus, and therefore has to be subsequently extracted, thus involving unnecessary operations. About 0·75% to 0·85% (245 ozs. to 277 ozs. 13 dwts. 8 grs. per ton) of silver in the ore-furnace lead is generally considered a proper proportion, when the silver in the regulus from the lead-smelting amounts to about 0·125% (40 ozs. 16 dwts. 16 grs. per ton), or somewhat more.

The products of the lead-smelting process are—

Werkbly (work-lead), or ore-furnace lead, in which is concentrated the greater proportion of the silver in the galena, and which contains an annual average of 0·86% (280 ozs. 18 dwts. 16 grs.) of silver.

Skärsten (regulus), derived partly from the iron-pyrites and blende which accompany the ore, and partly from the sulphide of iron produced from the sulphur in the galena. In consequence of the tendency of silver to combine with sulphur and metallic sulphides, the regulus always retains a small quantity of silver, usually about 0·125% (40 ozs. 16 dwts. 16 grs. per ton), but sometimes more. It always contains moreover sulphide of lead, the amount being dependent on the quality of the ore.

Slagg (slag), composed of singulo-silicates (*i.e.* tribasic), the bases being protoxide of iron, lime, magnesia, and alumina. This slag is used as a flux in both the lead- and the raw-smelting processes.

In addition to the two smelting processes above described, it is necessary to notice the following operations:—

Wändrostning (calcination). The regulus, or Skärsten, from both the raw- and the lead-smeltings, and the iron-pyrites required in the latter process, must undergo calcination in order to get rid of a portion of their sulphur. This roasting is commonly effected in brick-lined kilns (*murade rostgropar*), and the heap is turned over from time to time so as to be completely permeated by the heat. It is from this treatment that the operation derives its name of "Wändrostning" (turn-roasting).

Drifning af Werkblyet (cupelling the work-lead). The ore-furnace lead is cupelled by the German method with wood for fuel. The bottom is made of a finely-pulverized mixture of limestone and clay. The charge is 50 or 60 centners of metal. The Abstrich, which rarely amounts to 1 ctr. per charge, is removed from the surface with a hook, and is usually accompanied by a small quantity of lead. The oxide which is first formed is of a black colour, and contains a greater or less proportion of antimony and zinc, according to the nature of the ore. This is called antimonial or black litharge (*Antimon- eller Svart-Glete*), and should be carefully preserved for reduction as subsequently explained. [The blackness is probably due to the presence of a little copper.] At a later stage of the process yellow litharge alone is produced; the portions first formed contain but little silver, and may be reduced without further treatment, but towards the close of the operation this yellow litharge

contains a larger proportion of silver, and is then used in the lead-smelting. In addition to these oxides there is produced red or flake litharge (*Rödglete*), which forms a reddish-yellow scaly-crystalline substance, appearing beneath the yellow oxide or coarse litharge during cooling, and passing in commerce under the name of *Silfverglitt*. The silver is further refined by the German method, as it retains lead in small quantity, and most, it is stated, at the bottom of the cake. The bottom is broken up and treated in the ore-furnace.

Finering (refining). In this operation the silver from the cupelling-furnace (*Blicksilfver*) is refined so as to attain the degree of purity prescribed for delivery at the Government Mint. For this purpose it must contain at least 15 loods 15 grän of pure silver to each so-called "lödig mark," or pound of bullion—a proportion corresponding to 98·958%. This operation is conducted [with the aid of a blast] in two small reverberatory furnaces with hearths of a similar construction to that of the cupelling-furnace, but containing a little powdered bone-ash in admixture which gives a smoothness to the surface. A small quantity of lead is added in order to facilitate the melting, and the oxidation of the baser metals. After a few hours the refining is complete, and the ingot of fine silver (*Finplants*) is removed whilst still warm. The metal has now attained the requisite standard of purity, and is distinguished as *Bergfint* (mine-fine silver).

Friskning af Glete (reduction of the litharge).[4] The yellow oxide, or "coarse litharge" of English smelters (so-called not on account of impurities, but because it is in lumps), which is obtained in the early stages of cupellation, and which contains the smallest amount of silver, is reduced in a blast-furnace (*Schachtugn*) with the addition of a small quantity of slag to act as a flux; especially the slag from a previous fusion free from "Skärsten," and highly charged with oxide of lead. During the operation the melted lead must be continuously run off into a reservoir where it is kept heated by a coal-fire. Most of the impurities present are here removed, before the lead is transferred to a cast-iron kettle (*Tackjerns-kittel*) for the purpose of being refined. In this kettle the lead should be kept only just warm enough to prevent solidification, by which means certain metallic impurities present accumulate on the surface of the lead, and are from time to time skimmed off the surface, and the purified metal is cast into ingots. In this condition it is a *soft* lead, and passes in commerce under the name of *Friskbly*. At the end of the reduction, the slag and other furnace-products are collected for use in the smelting-furnace.

The black or antimonial litharge mentioned above is reduced in a similar manner, but it yields a *hard* lead, containing both antimony and zinc, which is occasionally used as [inferior?] type-metal. The

[4] The reduction of litharge will be separately described in the sequel; but in order to complete the description of the operations at Sala, a brief account of the method of reduction is given in this place.

slags resulting from its reduction have a peculiar character, and are kept apart from the others. The hard lead may be refined in the furnace used for cupelling: a large quantity of black litharge is produced, and the lead becomes much softer. If its yield of silver be sufficiently large, it may be cupelled in the ordinary way, but otherwise it is sold as "Friskbly."

The argentiferous galena of Sala is comparatively rich in silver, its produce of silver varying between 0·5% and 0·75% (163 ozs. 6 dwts. 16 grs. and 245 ozs. per ton) when the mineral is free from vein-stuff. Occasionally it has risen as high as 1% (326 ozs. 13 dwts. 8 grs. per ton), while on the contrary it has sometimes fallen as low as 0·25% (81 ozs. 13 dwts. 8 grs. per ton).

The total production of silver and lead at Sala in the year 1866 was as follows:—

Bergfint silfver, or refined silver for the Government Mint	1956 Swedish pounds.
Lead	1022 centners.
Silfverglitt, "flake litharge"	317

The number of workmen employed at Sala is upwards of 300.

Sala, 1st Oct., 1867.

LEAD-SMELTING AT FREIBERG.

The blast-furnace is employed for certain ores, and the reverberatory furnace for others, which are smelted along with the slags of the blast-furnace. The information on which the following description is founded has been derived for the most part from the lectures of Plattner, published posthumously, and ably edited by Professor Richter of Freiberg, who from his position should be one of the best living authorities on the subject.[1] As far as I have judged necessary I have translated literally. I have much pleasure in acknowledging my obligation to Richter for having examined the following description before publication, and added important notes, which will be found to be duly acknowledged. I have also availed myself of the lucid and well-arranged treatise of Winkler on the Freiberg smelting processes.[2] The smelting of lead is the chief metallurgical operation performed at Freiberg; and it includes the smelting of silver ores, molten lead being the vehicle in which the separated silver is collected.[3]

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[1] Vorlesungen über allgemeine Hüttenkunde. Von Carl Friedrich Plattner. Nach dem hinterlassenen MS. herausgegeben und vervollständigt von Theodor Richter. Freiberg, 1860. 2 vols. 8vo.

[2] Beschreibung der Freiberger Schmelzhüttenprozesse. Kurt Alexander Winkler. Freiberg, 1837. 8vo. One of the most recent and most methodic descriptions of the process will be found in the Annales des Mines, 6 ser. 1864. 6. p. 1, et seq. By M. Ad. Carnot, ingénieur des mines, of which description I have availed myself.

[3] The attention of lead-smelters and the public should be directed to the fact that a few years ago the Saxon Government practised the fraud of attaching the name of a great English lead-smelting firm to

The woodcuts (figs. 99 to 111 inclusive) representing the furnaces in use at Freiberg have been prepared from beautiful and well-known German lithographs.

Mode of occurrence and nature of the ores at Freiberg.—The ores smelted at Freiberg are obtained from lodes in a schistose gneiss formation, concerning the age of which the only point determined is that it is older than the carboniferous system. According to Von Herder more than 900 different lodes occur within the district, which may be divided into the following groups according to their relative ages, beginning with the most ancient, and which are characterized by the presence of particular minerals :—

I. The "Precious Quartz" group.
II. The "Pyritic Lead" group. The "Cupriferous" group is only a local modification of the preceding (II.).
III. The "Precious Lead" group.
IV. The "Barytic Lead" group.

I. *The precious quartz group.*—It includes about 150 lodes, varying from 6″ to 7′ in width. The vein-stuff consists almost wholly of quartz, with included fragments of the rocks traversed; and the ores occur in nests and drusy cavities very irregularly distributed. The metalliferous (so-called) mineral species are argentite, pyrargyrite, proustite, silver-fahlerz, miargyrite, polybasite, stephanite, argentiferous arsenical pyrites, antimonite (SbS^3), and kermesite ($SbO^3,2SbS^3$). At Bräunsdorf, where the lodes of this formation are best developed, they only bear well in a black carbonaceous schist and become poor when they pass into the adjacent mica-schist.

II. *The pyritic lead group.*—It includes about 300 lodes, varying from 2″ to 3′ in width, and mostly to the south-east of Freiberg; and amongst them are the lodes belonging to the Himmelfahrt Mine, one of the largest and most important mines in Europe. The vein-stuff consists chiefly of quartz, with spathic carbonates, sulphate of baryta, and fluor-spar. The metalliferous mineral species are galena, containing from 10 to 60 ozs. of silver per ton of lead, zinc-blende, iron-pyrites, copper-pyrites, mispickel, and most of the silver ores previously enumerated. These lodes generally carry a strong gozzan.

The principal localities of the *cupriferous group* are at the Morgenstern and Jungehohebirke Mines. The vein-stuff is quartz, and the metalliferous mineral species are copper-pyrites, purple copper-ore, vitreous copper (Cu^2S), fahlerz, red and black oxides of copper, and blue and green carbonates of copper.

III. *The precious lead group.*—It includes 340 lodes, which occur

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the shot manufactured by that Government. My friend, Mr. Alfred Walker, a member of that firm, has communicated to me, for publication, the following statement on the subject. "In the year 1856 I was at Freiberg, and on visiting the shot manufactory I found that nearly all the bags of shot were sent out with the name of Walkers, Parker and Co., Newcastle-on-Tyne, printed on their bags. This shot manufactory was under Government management, as shown by the inscription over the door, 'Königliche Sächsische Schrotgiesserei.' "

principally in the neighbourhood of Brand and Erbisdorf. The vein-stuff consists chiefly of spathic carbonates, especially brown-spar, diallogite, and quartz. The metalliferous mineral species are galena, richer in silver than that of the *pyritic lead formation*, blende, and iron-pyrites, which are often arranged in symmetrical layers, with native silver and silver ores in small quantity. The principal mines on these lodes are the Bescheert Glück and the Himmelfürst.

IV. *The barytic lead group.*—It includes 130 lodes, some of which are of great size and are remarkable for the parallel or banded structure of the filling. Beautiful examples of this occur in the famous Drei Prinzen Spat of the Kurprinz Mine. The vein-stuff consists principally of sulphate of baryta in layers parallel to the walls, with subordinate layers of galena, blende, iron-pyrites, fluor-spar, and quartz; and large drusy cavities are occasionally found, which contain the same minerals, with silver ores and spathic carbonates, often beautifully crystallized. A brecciated structure, due to successive re-openings of the vein-fractures, is common in the larger lodes.

Classification of ores.—The lead ores at Freiberg are divided into two classes, which I will designate A and B, the former (*Glanze* or bright ores) by far the most abundant, containing 30% of lead and upwards, and the latter (*bleiische Erze* or leady ores), containing from 15% to 29%. The lead exists wholly as galena, associated with iron-pyrites, mispickel (FeS^2+FeAs), zinc-blende and earthy matters (so-called) of which the chief are quartz, calc-spar, brown-spar ($CaO,CO^2+(MgFe)O,CO^2$), and heavy-spar or sulphate of baryta. The average yield of all the lead ores is 40% of lead and 0·15% (49 ozs. per ton) of silver, *i.e.* 0·375% in the lead or 122 ozs. 10 dwts. per ton. Other argentiferous ores raised at Freiberg are divided into three classes, which I will designate C, D, E, and these are smelted along with the lead ores. Class C (*Dürrerze* or dry ores) consist occasionally almost entirely of vein-stuff, but very often contain iron-pyrites and small quantities of galena: the yield of silver in these ores ranges from 0·05% (16 ozs 6 dwts. 16 grs. per ton) to 0·1%; and when it exceeds 0·10% (32 ozs. 13 dwts. 8 grs. per ton), they are smelted in the blast-furnace, but when it is below that percentage they are smelted along with lead-slags in the reverberatory furnace. Class D (*Kupfererze* or copper ores) contain from 1% to 10%, and on the average 3%, of copper: a large portion of these ores, on account of their high content of silver, are smelted along with the lead ores, but in that case the proportion of copper should not exceed 6%. Class E (*Zuschlagserze*) contain less than 0·03% (9 ozs. 16 dwts. per ton) of silver, and are chiefly composed of iron-pyrites, mispickel, zinc-blende often in considerable quantity, quartz and calc-spar, with some lead and copper diffused throughout.

Mixture of ores.—The quantity of ore mixed at a time for smelting (*i.e.* without fluxes, &c.) usually amounts to from 75 to 100 metrical tons (1 centner = 50 kilogrammes, and 1 metrical ton = 20 centners), and is composed of about 60% of A, about 20% of B, and 20% of a mix-

ture of C and D. The proportion of lead in such a mixture ranges between 34% and 38%, and the proportion of silver between 0·15% and 0·18% (49 ozs. and 58 ozs. 16 dwts. per ton). The composition necessarily varies from time to time according to the quantities of the different kinds of ore delivered at the smelting works.

Operations in the Freiberg Process.

The Freiberg process of lead-smelting is somewhat complicated; but the following introductory remarks will, it is hoped, assist the reader in his study of the detailed description of it presently to be given. The metals, which are the chief objects of extraction, are lead and silver; and upon them attention should be concentrated. Copper and a little nickel are also extracted; but these may be regarded as accessory products. The process consists of three principal operations, namely:—

I. Smelting certain Ores in Blast-Furnaces.
II. Smelting in Blast-Furnaces the Regulus produced in that operation (I.).
III. Smelting Slags, containing Lead, in conjunction with certain Ores in Reverberatory Furnaces.

I. *Smelting certain ores in blast-furnaces.*—The ore is calcined or roasted with access of atmospheric air, until not more than 5% of sulphur is left in it. The *calcined ore* is smelted in blast-furnaces in admixture with *roasted regulus*, derived from slags previously obtained from the same furnaces in similar smelting operations. The products are *lead*, *regulus*, and *slag*. The regulus will be designated *blast-furnace regulus*: it is the *Bleistein* of the Germans. It contains on the average 20% of lead, 10% of copper, and 0·2% of silver, and is the subject of treatment in Operation II. The slag contains a notable quantity of lead, and is the subject of treatment in Operation III.

II. *Smelting in blast-furnaces the regulus produced in Operation I.*—It is calcined and smelted in conjunction with certain *ores containing copper and silver*, fluor-spar, slags derived from previous similar smeltings of this regulus, and other slags holding lead. The products are *lead*, *regulus*, and *slag*. This *second regulus* contains 25% of lead, and 36% of copper, and the slag 2·5% of protoxide of lead. The regulus is calcined and treated in the same manner as *blast-furnace regulus*. The products are *lead*, *regulus*, and *slag*. This *third regulus* contains about 12% of lead, and 54% of copper. The regulus is calcined and smelted. The products are some *rich argentiferous lead*, *regulus*, and *slag*. This *fourth regulus* contains about 70% of copper, and is subjected to special treatment by *wet* or *dry* methods, or by a combination of both.

III. *Smelting slags, containing lead, in conjunction with certain ores in reverberatory furnaces.*—The products are *regulus* and *slag*. The regulus will be designated *reverberatory-furnace regulus*: it is the *Rohstein* of the Germans. It contains about 7% of lead, and 4% of copper, and is the same regulus as is smelted in Operation I. The slag is stated to contain 1·34% of lead, and is thrown away.

Ore-roasting or Calcining.[4]

The ore is roasted in flat-bottomed reverberatory calciners, each having two beds, one built over the other. The upper bed is constructed like a muffle; so that the gaseous products of the fuel should not pass over it and intermingle with those evolved from the ore; and it was designed with a view to apply the sulphurous acid generated in the process of roasting to the manufacture of sulphuric acid. The bottom of this bed is made of large fire-brick slabs resting upon three arches thrown across the lower bed, of which it forms the roof. The upper bed was heated exclusively on the exterior,—at the bottom by the bed underneath, and round the sides by flues; and it was connected with a sulphuric acid chamber. The scheme did not answer, and has been abandoned accordingly; but these furnaces are used in the ordinary manner for roasting, the gaseous products of the combustion of the fuel now passing over the upper as well as the lower bed.[5] The lower bed is 10′ long and 5′ 6″ wide; and the upper bed 13′ long and 6′ wide. (Saxon measure: 100 Saxon feet = 92·912 English feet.)

The charge is 10 ctrs. The ore is first roasted on the upper bed during 4 hours at a dull red-heat, and remains quite pulverulent without sintering: it is then transferred to the lower bed and roasted at a stronger heat during 4 hours more, whereby it becomes clotted into lumps. The sulphur in the roasted ore should not exceed 5%; and a determination of the sulphur is accordingly made as quickly as practicable. Of the roasted ore 1 gramme is mixed with 2 grammes of dry carbonate of soda and 2 grammes of nitre, both perfectly free from sulphuric acid: the mixture is melted in an iron capsule during 5 or 8 minutes in a muffle. The product is dissolved in hot water, and the solution is filtered and heated with hydrochloric acid in excess until nitrous gas ceases to be evolved; after which the proportion of sulphuric acid is found by a test liquor containing chloride of barium.

On the subject of roasting or calcining the following note has been added by Richter. The roasting or calcination of lead ores is at present conducted in what are called "Sinter-calciners" (*Sinterröstöfen*), which have two beds, one over the other, and only a single fire-place at one end of the lower bed. At the other end of this bed the flame passes through a hole in the arch to the upper bed, and thence directly over that bed to the flue. Through that hole the ore after calcination on the upper bed is transferred to the lower one. Each bed is 39′ long and 6·5′ wide, and the height to the roof is 18″. The fire-place is 4·5′ long and 20″ wide. There are eight working doors to each bed. On each bed 4 charges, of 10 centners each, are constantly in process of roasting or calcination at the same time, so that the whole furnace contains 80 centners. The ore is advanced at intervals of 2 hours and

[4] In the following description the words roasting and calcining will be used as synonymous, whereas in the Welsh process of copper-smelting they are applied to different operations.

[5] Carnot, op. cit.

in charges of 10 centners each, from the place of its entrance towards that of its exit, whereby it is subjected to a gradually increasing temperature. The charge which has been longest in the furnace being withdrawn, its place is filled with the charge next in order, and so in succession through the entire furnace. Thus each charge undergoes calcination during 16 hours. The temperature should be kept high enough to cause the charges near the fire-bridge to sinter strongly and become somewhat pasty, in which state they are fitted for the smelting process. Each furnace requires four men, and consumes 28 centners of coal per 24 hours. The calcined ore ought not to contain more than 5% of sulphur.

The regulus is stamped to powder and roasted in the furnaces above described; or, it is broken into pieces about as large as the fist and roasted in kilns, undergoing two or three firings. Well-roasted regulus has a grey-black, budlike (*knospig*), dull aspect, and consists chiefly of magnetic oxide of iron, with oxides of lead, copper, and zinc. The sulphur in it amounts at the most to 1% or 2%, and much of it exists as sulphuric acid in combination.

According to Carnot it is only the pyritic ores in lumps and the regulus produced in the smelting of lead-slags that are roasted in heaps or in kilns.[6] The heaps may be constructed just like the open coke-fires, with a central brick chimney, described in the first volume of this work.

Composition of roasted ore.—Mrázek has published the following analysis made by himself of a sample taken for the purpose of a sulphur assay from a melted portion of roasted ore from a double-bedded roasting-furnace at Freiberg in 1865: it resembled externally slag rich in protoxide of iron.[7] This ore, judging from the proportion of lead in it, must have belonged to Class B.

Composition of Roasted Ore.

Silica	17·4
Alumina	1·8
Lime	2·0
Magnesia	0·5
Oxide of iron *	33·3
Protoxide of manganese	trace
Oxide of zinc	16·0
Protoxide of lead	22·0
Protoxide of copper (CuO)	0·3
Antimonic acid	trace
Arsenic acid	1·1
Sulphuric acid	trace
Sulphur in sulphides	3·62
Silver	0·13
	98·15

* Almost exactly magnetic oxide of iron (Fe^3O^4).

[6] Carnot, op. cit. p. 22.

[7] Berg- und hüttenm. Jahrbuch, 1867, 16. p. 397.

Smelting in the Blast-Furnace.

Description of the Blast-furnace.—It is represented in the annexed woodcuts (figs. 99 to 104 inclusive).

a. Principal drain (*Hauptanzucht*).
b b. Cross-drains (*Kreuzanzüchte*).
c. The foundation wall (*Grundmauer*).
d. Back-wall (*Brandmauer*).
e. Side piers (*Seitenpfeiler*).
f. Refractory lining (*Futtermauer*).
g. Fore-wall (*Stern- oder Vorwand*).
h. Shaft (*Schachträume*).
i. Hearth (*Schmelzraum*).
k k. Twyers (*Formen*). The axes are somewhat convergent, and incline a little downwards.
l. Arch over the twyer-holes (*Formgewölbe*).
m. Slag-gutter (*Schlackentrift*).
n. Dam-plate (*Vorherdplatte*).
o. Slag-bottom (*Schlackengrund*).
p. Clay-bed (*Lehmsohle*).
q. Brasque-bed (*Gestübesohle*).
r. Hearth-bottom (*Spur*).
s. Dam (*Damm*).
t. Fore-hearth (*Vorherd*).
u. Tap-hole (*Stich, Stichkanal, Stichloch*).
v. Tap-bed, or cavity for tapping into (*Stichherd*).
w. Breast (*Brust, Brustwand*).
x. Draw-holes (*Zuglöcher*), through which an iron bar may be passed when necessary to detach adherent matter, assist the descent of the charge, etc. The two lower ones are on the same level as the twyers, and remain constantly open, while the upper ones are closed with moveable bricks during the working of the furnace.
y. Wall or tongue (*Zunge*), dividing the shaft.
z. Charging-holes (*Aufgebeöffnungen*).

The blast is produced by blowing cylinders, some of which are moved by turbines and others by steam power; it escapes at a pressure equal to 0^m 026 (1·03″) of a column of mercury.

These furnaces are for the most part built of gneiss.

Process of smelting.—The roasted ore is smelted with the addition of roasted regulus (*Rohstein*), from slag- and ore-smelting in the reverberatory furnace (see p. 319), lime or fluor-spar, slags produced in this process, and lead products, such as cupellation-furnace bottoms and litharge. When there is a deficiency of pyrites in the lead ores the stamped lead-regulus is roasted under the former. The lime is used caustic, and experience has shown that when so used the yield of lead is larger and the regulus and slag are poorer in lead.

The smelting-mixture is made near the mouth of the furnace in successive layers, one over the other, in the following order: roasted regulus, roasted lead ores, the residual silver-rich ores of Class C, lime or fluor-spar, and slags. The lead-regulus ranges generally from 30% to 40% of the weight of the ore. As a rule the mixture for smelting is composed of 60 ctrs. of ore (1 centner = 50 kilogrammes, say, about 1 cwt. avoirdupois), 20 ctrs. of lead-regulus, 2½ ctrs. of fluor-spar or lime, and constantly from 1¼ to 1½ ctr. of slags to 1 ctr. of ore, that is, the quantity sufficient to supply one furnace during 24 hours (*Bleiarbeitsschicht*).

The fuel used is exclusively coke, containing about 22% of ash, made from carboniferous coal raised in the Plauensche Grund near Dresden.

The smelting is conducted with a *nose* (*i.e.* a slag prolongation of the twyer) and without flame at the mouth (*mit dunkler Gicht*). The

furnace is charged so that the mixture of ore and flux is thrown towards the back-wall and the fuel towards the fore-wall. The proportion of coke is mainly determined by the character of the nose, and should be relatively increased or decreased according as the nose is too long or too short: it should be from 4″ to 6″ long.

The lead products are specially required when rich silver ores of Class C form part of the charge, and are only thrown in at the angles of the back-wall shortly before tapping. Each furnace receives in 24 hours about 3 ctrs. of litharge or 4 ctrs. of hearth-bottoms. When

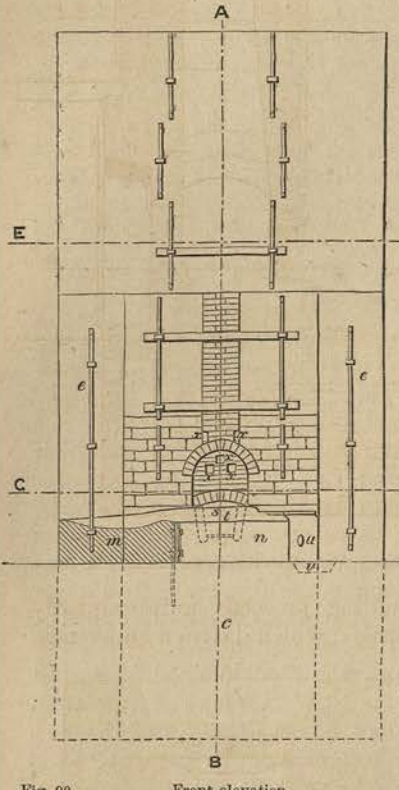

Fig. 99. Front elevation.

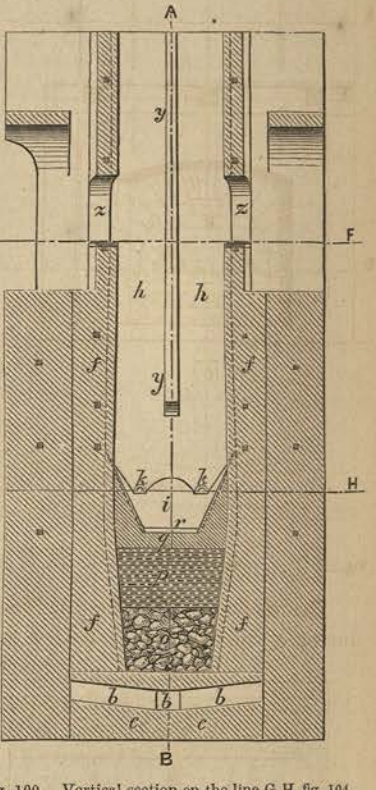

Fig. 100. Vertical section on the line G H, fig. 104.

the charge is poor in silver the addition of these products may be omitted with advantage.

In such a furnace are daily smelted on the average 60 ctrs. of ore. 20 ctrs. of lead-regulus, and from 90 to 100 ctrs. of slags from this furnace, with a consumption of from 24 to 27 ctrs. of coke.

Three men are required at a furnace, a smelter and an assistant, and a labourer. A shift lasts 12 hours. There are usually four tappings in 24 hours. The tap-hole is stopped with clay. A little regulus is always left behind in the bottom of the hearth in order to

prevent the accretion of other matters, such as slag, etc., upon it. The slag is not allowed to run constantly, but is frequently tapped.

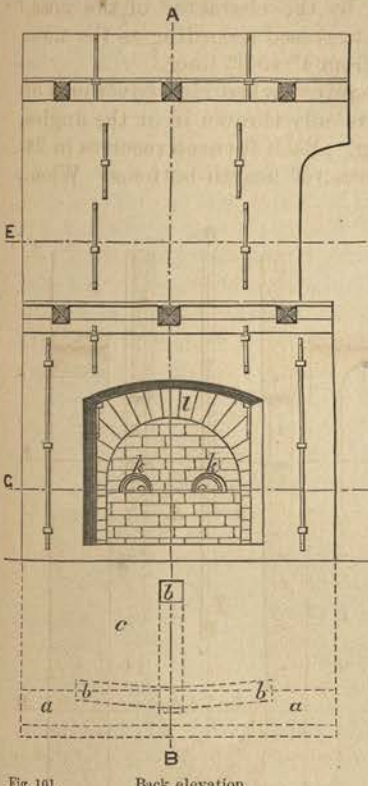

Fig. 101. Back elevation.

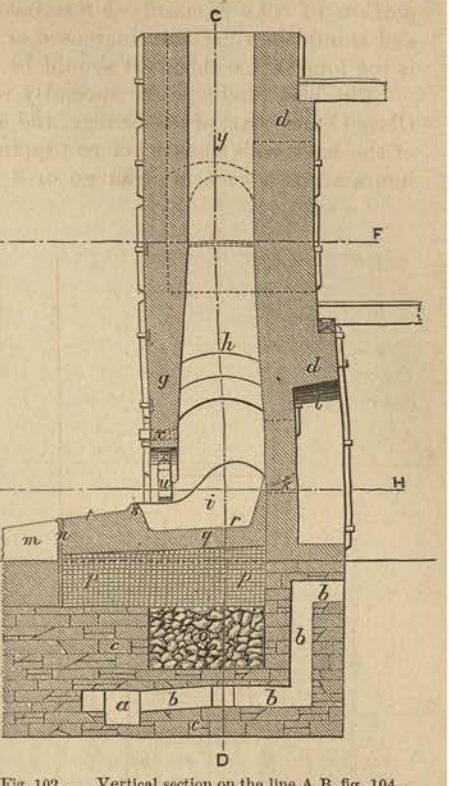

Fig. 102. Vertical section on the line A B, fig. 104.

Duration of the smelting.—The smelting proceeds uninteruptedly during a limited period, called a *campaign*, which lasts on an average

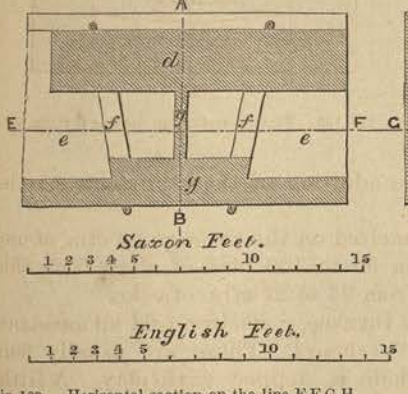

Fig. 103. Horizontal section on the line E F G H, figs. 99, 100.

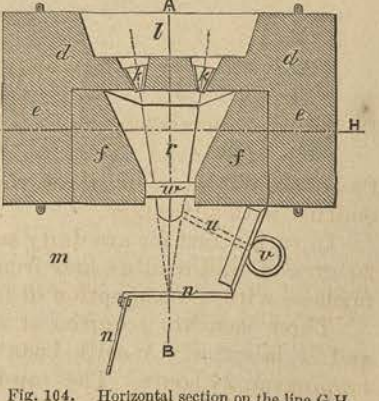

Fig. 104. Horizontal section on the line G H, figs. 99, 100.

about 10 weeks ; and then follows the treatment of the regulus produced in that campaign, mainly with the object of extracting from it argentiferous lead, slagging off iron, and concentrating the copper in a fresh regulus.

Products.—The products of tapping are blast-furnace lead (*Werkblei* or work-lead), lead-regulus (*Bleistein*),—which, in order to distinguish it from the regulus produced in the reverberatory furnace (see p. 323), will be designated *blast-furnace regulus*,—and not rarely speise (which chiefly consists of iron and arsenic and will hereafter be described), and slag; the regulus solidifies on the lead, and is taken off in a cake, but the slag which may have solidified upon the regulus is first removed. The lead is laded into moulds in the usual manner.

Blast-furnace lead.—The average yield at each tapping is 4 ctrs., containing from 0·50% to 0·60% (163 ozs. 6 dwts. 16 grs. to 196 ozs. per ton) of silver. The mean composition of the blast-furnace lead from the two Government Smelting Works at Freiberg has been determined by Professor Richter, and is stated underneath :—

Composition of Blast-Furnace Lead.

	Mulde Works.	Halsbrücke Works.
Lead	97·56	96·69
Silver	0·45	0·53
Copper	0·59	0·20
Iron	0·07	0·06
Arsenic, Antimony	1·52	1·30, 0·71
	100·19	99·49

The blast-furnace lead is softened or refined (*raffinirt*) in a reverberatory furnace, Pattinsonized so as to give enriched lead containing double the percentage of silver, and then cupelled. A specimen of refined lead (softened and not Pattinsonized) from the Mulde Works has been found by Richter to have the following composition :—

Composition of softened Blast-Furnace Lead.

Lead	98·46
Silver	0·64
Copper	0·22
Iron	0·05
Arsenic	0·14
Antimony	0·30
	99·81

Blast-furnace regulus.—The average production of regulus at each tapping is 2 ctrs.; it contains on the average 20% of lead, 10% of copper, and 0·20% (65 ozs. 6 dwts. 16 grs. per ton) of silver. The following analyses of this regulus have been made by Plattner :—

COMPOSITION OF BLAST-FURNACE REGULUS.

	I.	II.	III.	IV.
Sulphur	21·314	19·852	22·847	17·55
Lead	20·250	23·288	21·816	31·10
Iron	27·051	36·017	37·202	37·47
Copper	27·614	15·277	12·944	4·81
Nickel	1·010	2·329	0·544	1·96*
Zinc	0·231	0·136	1·439	2·75
Silver	0·117	0·121	0·099	0·14
Arsenic	0·650	1·248	0·731	1·28
Antimony	1·005	0·849	0·718	1·00
Carbon	..	..	..	1·20
	99·242	99·117	98·340	99·26

* Inclusive of cobalt.

I. Blast-furnace regulus re-smelted, from the Mulde Works. II. Re-smelted reverberatory-furnace regulus, presently to be described, from the Mulde Works. III. Re-smelted blast-furnace regulus, from the Halsbrücke Works. IV. Regulus directly obtained in the smelting of nickeliferous and cobaltiferous ores at the Halsbrücke Works. The carbon in No. IV. it is conjectured, was chemically combined with iron.

The re-smelting above mentioned under Nos. I., II., III., is termed "Verändern." The charge in this process consists usually of 20 ctrs. of stamped and roasted blast-furnace regulus, 80 ctrs. of slags produced in the same process, and of various matters containing lead, such as furnace accretions, &c. (*Geschur*), but not litharge or hearth-bottoms. The smelting is effected in the blast-furnace, and from 7 to 9 tappings are made in 24 hours. The products are argentiferous lead, such regulus as Nos. I., II., III., and slags. The treatment of this regulus is described at p. 316. By comparing the composition of the regulus No. IV. with that of Nos. I., II., III., it will be seen that the object of the process in question is the separation of argentiferous lead and the formation of regulus less rich in lead and silver, but richer in copper.

Speise.—A speise often occurs as a thin crust between the regulus and the lead; it is crystalline, largely foliated, very brittle, and yellowish-white; it consists chiefly of arsenide of iron, but contains some nickel and cobalt and is mixed with sulphides of iron, copper, lead and zinc; it is also argentiferous, and may be easily and completely detached from the regulus. It is collected, roasted, and smelted with lead products in order to extract its silver; and in this process a speise, richer in nickel and cobalt, lead-regulus, and lead are obtained. The last two of these products go back to the blast-furnace, while the speise is treated for nickel and cobalt.

Slags.—Of the total charge of lead and silver-yielding materials, inclusive of flux, about 73% of slag are produced, containing from 5% to 6% of lead and about 0·02% (6 ozs. 10 dwts. 16 grs. per ton) of

silver. These slags are black and have a feebly metallic lustre, resembling those produced in the treatment of pig-iron in the charcoal-finery and puddling-furnace. Their specific gravity varies from 3·8 to 4·1.

COMPOSITION OF BLAST-FURNACE SLAGS.

	I.	II.	III.	IV.
Silica	35·16	43·26	28·14	27·05
Alumina	1·06	3·20	5·78	6·85
Protoxide of iron	38·25	33·15	37·23	41·21
Lime	5·96[1]	5·41	7·68	8·84
Baryta	..	..	3·87[4]	..
Magnesia	..	0·71[3]	0·63[3]	0·90[3]
Protoxide of lead	7·11	5·64	7·35	3·90
Oxide of zinc	8·06	7·83	7·60	8·62
Protoxide of copper	0·73	0·61	0·50	1·00
Sulphur	3·30[2]	0·32	2·47	3·53
	99·63	100·13	101·25	101·90

[1] Inclusive of a little magnesia.
[2] Inclusive of some coke.
[3] Inclusive of some protoxide of manganese.
[4] Assumed to exist as sulphide of barium.

I. II. By Plattner from the Mulde Works. III. By Richter, in an analysis of an average sample of a large quantity of slag from the Halsbrücke Works. IV. By Richter, in an analysis of an average sample of a large quantity of slag from the Halsbrücke Works.

Taking No. IV. as a fair sample of the slag, and assuming the sulphur to be in combination with calcium, as protosulphide (CaS), the oxygen of the bases of the RO type amounts to 11·75, while that of the base of the R^2O^3 type, *i.e.* alumina, is 3·20, and that of the silica 14·05. The sum of the oxygen of both types of bases is 14·95. The slag, therefore, has nearly the formula of tribasic silicate, *i.e.* of silicate in which the oxygen of the silica is equal to that of the bases; and as the oxygen of the bases of the RO type is to that of the alumina as 11·75 : 3·20, the constitution of this slag may approximately be represented by the formula $Al^2O^3,SiO^3+4\,(3RO,SiO^3)$.

The slag, it need hardly be remarked, is seldom quite free from mechanically intermingled regulus; and the zinc, it is suggested, may in part be present as oxide and in part as sulphide.

Other kinds of blast-furnace now in use at Freiberg, 1868. *Note by Richter.*—The smelting of the roasted lead ores is at present conducted not only in the furnaces above described, but also in the *Stolberg furnace* and in the "seven-twyer furnace" (*Siebenförmiger Ofen*): the latter will in all probability be exclusively used in future.

Stolberg furnace.—The hearth is trapezoidal in horizontal section, like that of the furnace last described (see fig. 103); at the level of the twyers the back-wall is 4′ 8″ wide, and the front-wall 2′ 3″, in-

side measure; there are four water-twyers, set as usual at the back, not parallel, but so that lines in the direction of their axes would converge in the middle of the upper and anterior edge of the fore-hearth; the fore-hearth extends 1′ in front of the fore-wall; the depth of the hearth below the twyers is 2′; the height from the twyers to the bottom of the charging-hole, which is in the back-wall, is 12′ 10″; the fore-wall and back-wall are parallel, and the distance between them is 2′ 6″. One of these furnaces will smelt in 24 hours about 200 centners of roasted lead ore, 100 centners of roasted regulus, 10 centners of lime, and about 350 centners of rich lead-slags, with a consumption of 66 centners of coke: the materials, therefore, require one-tenth of their weight of fuel. The slags contain from 0·0025% to 0·003% (16 dwts. 8 grs. to 19 dwts. 14 grs. per ton) of silver, and 2% of lead.

Seven-twyer furnace.—It is constructed on the principle of the Sefström furnace. It has a cylindrical shaft and an octagonal outer-casing: its principal dimensions are as follow:—

	Feet.	Inches.
Diameter across the plane of the twyers (*Formebene*)...	5	6
Ditto at the mouth (*Gicht*)	7	6
Height from twyers to mouth.....	20	0
Depth of hearth (*Sumpf*)	2	2

The furnace is provided with seven water-twyers, one being placed in the centre of each of seven sides of the octagon, and the fore-hearth being situated on the eighth side. Each nozzle is 2·5″ in diameter, and the total amount of air injected per minute is about 800 cubic feet at the ordinary atmospheric pressure. The mouth is provided with charging apparatus, such as is used in iron-smelting furnaces. The slag does not flow out uninterruptedly, but is tapped off, as occasion may require, into a cast-iron pot through two openings which are usually kept closed. When the furnace is in ordinary working condition, the slags contain from 0·001% to 0·0025% (6 dwts. 13 grs. to 19 dwts. 14 grs. per ton) of silver, and from 0·5% to 1·5% of lead. One of these seven-twyer furnaces will smelt in 24 hours the following quantities:—

	Centners.
Lead ore.....	370
Roasted regulus	150
Lead residues (skimmings, etc.—*Bleigekrätz*) ...	40
Lime	20
Slags	320
	900

The consumption of coke is about 90 centners.

The analysis of a slag from the furnace in its normal working condition gave the following results:—

Composition of Slag.

Silica	32·50
Alumina	2·13
Protoxide of iron	40·00
Protoxide of manganese	3·51
Lime	4·95
Magnesia	0·97
Baryta	4·46
Protoxide of lead	0·99
Dioxide of copper	0·22
Oxide of zinc	8·50
Sulphur	2·18
	100·41
Oxygen equivalent to the sulphur*	1·09
	99·32

* It is not known how the sulphur is distributed, and therefore an equivalent of oxygen must be deducted.

Lead-smelting in a seven-twyer blast-furnace in the Harz.—It is an interesting historical fact that a furnace of this kind was erected in the Harz by Von Reden nearly a century ago. It appears to have been rectangular, and was 36′ high and 14′ wide at the boshes; the hearth was nearly square in horizontal section, its dimensions being 7′ by 6½′. There were seven twyers and four bellows, from which the air, in its course to the furnace, passed into a larger bellows weighted on the top, and thus acting as a regulator. The result is stated to have been very satisfactory: the daily yield was 160 centners of lead; the quantity of regulus formed was much smaller than previously, containing only from 6% to 8% of lead; and the slag contained from 1½% to 2% of lead free from silver. But, owing to the difficulty of producing adequate blast, and making the hearth sufficiently refractory, lead-smelting in this furnace was abandoned.[8]

Smelting of Regulus.

First smelting.—The same kind of blast-furnace is used, but the twyers in this case are placed perfectly horizontal. The proportions of a smelting-charge are stated to be as follow[9]:—roasted blast-furnace regulus 100, roasted ores (copper ores) of Class D 20, slags obtained in the reduction or revivification of litharge 24, fluor-spar 4, and slags from the same operation from 50 to 60. About 110 ctrs. of regulus are passed through the furnace in 24 hours, with a consumption of 35 bushels of coke (Dresden, of which 1 = 2·89 English bushels), the production being about 18 or 20 ctrs. of coppery lead, containing 0·75% (245 ozs. per ton) of silver, and 30 ctrs. of copper-regulus, containing on an average 30% of copper and 0·18% (58 ozs. 16 dwts. per ton) of silver. There is also a little speise consisting chiefly of arsenide of iron, with some nickel and cobalt: it occurs between the regulus and the lead.

[8] Bergmännisches Journal, Freiberg, 1788, pp. 775 and 842.

[9] Carnot. op. cit. p. 65.

COMPOSITION OF THE COPPER-REGULUS.

Sulphur	21·00
Lead	24·80
Iron	15·20
Copper	36·20
Silver	0·16
Nickel, zinc, antimony, inclusive of loss	2·64
	100·00

From the Halsbrücke Works. Analysis by Ihle.

COMPOSITION OF THE ACCOMPANYING SLAG.

Silica	28·05
Alumina	4·33
Protoxide of iron	61·08
Lime	3·02
Magnesia	0·85
Protoxide of lead with traces of copper	2·67
Sulphur not determined	..
	100·00

Analysis by Brooks in Rammelsberg's laboratory.[10] This agrees with the formula of tribasic silicate.

Second smelting.[11]—The last copper-regulus is stamped, roasted, and re-smelted under conditions nearly identical with those of blast-furnace regulus. This operation generally ends the campaign of regulus-smelting, which lasts from 12 to 14 weeks. The roasted regulus is smelted along with a small quantity of coppery ores of Class E, fluor-spar, slags from the revivification of litharge or those from the concentration smelting of coppery regulus in the reverberatory furnace. The products are impure lead, rich regulus (*Spurstein*), black-copper rich in lead, coppery speise, and slag. The lead is softened and then desilverized.

COMPOSITION OF THE REGULUS.

Sulphur	18·01
Lead	12·32
Iron	10·39
Copper	53·88
Nickel, cobalt, zinc	1·18
Arsenic, antimony	1·53
	97·31

Analysis by Reich.

The treatment of this regulus is given in the sequel, p. 333.

The coppery lead of this second smelting is repassed, towards the end of the campaign, through the same furnaces along with reguluses and coppery pyrites, slags from the revivification of litharge,

[10] Lehrb. der chem. Metallurg. 2nd ed. 1865, p. 247. [11] Carnot. op. cit. p. 67.

1% of fluor-spar, and 3% of sulphate of baryta; and in this way a rich copper-regulus is obtained.[1]

The speise is rich in copper, containing, it may be, 40%, with 10% of lead, 2·5% of nickel and cobalt, and 0·5% of silver or about 163 ozs. per ton. It is smelted with 50% of hearth-bottoms of the cupellation-furnace, 150% of barytic slags, formed in the *concentration* of copper-regulus in the reverberatory furnace by fusion with sulphate of baryta and silica,[2] and 10% of sulphate of baryta, whereby are produced speise containing 12% of nickel and cobalt, regulus rich in copper, and argentiferous lead. This speise and others of about the same richness from preceding operations, are smelted altogether in a blast-furnace with about 400% of litharge and 300% of slags from the revivification of litharge, and 10% of sulphate of baryta; and a second speise is thus procured which is again smelted in the same furnace along with 10% of sulphate of baryta and 300% of rich slags formed in this second treatment of speise. The final product is a desilverized speise containing 18% of copper, 12·65% of nickel, 1·84% of cobalt, and 0·03% of silver or about 9½ ozs. of silver per ton. Each smelting operation yields lead, which is refined, and copper-regulus. The speise is further enriched by smelting it in a small reverberatory furnace with 50% or 60% of sulphate of baryta and 20% or 25% of quartz. After this treatment it contains from 40% to 44% of nickel and cobalt.[3] The explanation of this process of concentrating nickel and cobalt in the speise will be given hereafter in the metallurgy of those metals. Suffice it here to remark that the action is analogous to what occurs in copper-smelting, *mutatis mutandis*, arsenic being substituted for sulphur, and nickel and cobalt for copper.

Slags from regulus-smelting.—No distinction is made between those of the first and second smeltings. They are treated along with ores of Class E in the reverberatory furnace, precisely in the same way as those from ore-smelting in the blast-furnace. The composition of a regulus produced from such slags is as follows:—

Composition of Regulus.

Sulphur	21·81
Lead	5·69
Iron	51·33
Copper	11·33
Zinc*	2·14
Arsenic, antimony	0·73
Oxygen and loss	6·97
	100·00

* Inclusive of traces of cobalt and manganese.

Analysis by Richter.

[1] Carnot. op. cit. p. 68.

[2] Plattner, Allgem. Hüttenk. 2. p. 196.

[3] Carnot. op. cit.

Smelting of Lead-Slags.

This process is in fact slag and ore-smelting combined. The ores treated are those of the Classes C and E, together with all the slags produced in the operations previously described. It would be scarcely possible to smelt profitably by themselves such considerable quantities of these ores, which are frequently very siliceous, as are delivered at the Freiberg Works; but by admixture with highly basic lead-slags, sufficient base is supplied by the latter to flux the silica of the former, and a regulus is obtained, which constitutes the most important addition to the ore in the smelting in the blast-furnace. The smelting is now conducted in reverberatory furnaces, and not as formerly, at the end of a campaign of smelting ore in the blast-furnace, in the same blast-furnace as used in that campaign. The object in roasting a portion of the ores treated in lead-slag-smelting is to prevent the formation of too much, and consequently too poor, regulus, as well as to avoid the production of too refractory slags from the high content of zinc in the ores of the Classes C and E. Ores of Class C poor in pyrites are not roasted.

Roasting.—This operation may be conducted in a furnace like an ordinary Welsh copper ore calciner.

Description of the reverberatory smelting-furnace (figs. 105 to 111 inclusive):—

a a. Foundation walls (*Grundmauer*).
b b. Cast-iron plates carrying the bed of the furnace.
c c. Pillars on which the plate *b b* rests.
d d. Outer walls or casing of hard burnt brick.
e e. Fire-place.
f. Grate.
g. Fire-hole.
h h. Fire-bridge of fire-brick.
i. Openings for the circulation of air through the fire-bridge in order to keep it cool.
k. Refractory lining, composed of an intimate mixture of calcined quartz and clay.
l l. Roof of fire-brick.
m m. Brick bottom.
n n. Layer, composed of a mixture of quartz and fire-clay immediately under the bed, strictly so called, which is formed by melting over the layer *m m* a mixture of quartz and blast-furnace slag.
o. Openings for the admission of air.
p. Working door, through which the slag is skimmed off.
q, r. Side openings provided with moveable doors.
s. Tap-hole.
t. Charging-hole in the roof.
u. Iron bar for resting the working tools upon.
v. Iron bar for supporting the tools used in clinkering.
w. Flue.
x. Chimney of hard-burnt bricks, solidly lined with a mixture of quartz and clay.

The furnace, as well as the chimney, is strongly braced with wrought-iron tie-rods, over cast-iron plates.

On the working side of the furnace the floor of the smelting-house is covered with coarse moist sand, in which are made several hemispherical cavities for the reception of the slag. Usually there are also several ingot-moulds of iron, formed of two rectangular parts, open at the top, and closed at the bottom by the sand on which they stand; and into these the slag which is intended for building purposes is allowed to flow. The masses of slag thus obtained are 2′ long,

1′ broad, and 1′ high. In front of the tap-hole are several rectangular ingot-moulds of iron, of the form of an inverted truncated pyramid, in which the regulus is received. These are placed in a row, side by side, and by means of notches the molten mass can overflow from one mould into the adjoining one, and so in succession into the others. Hooks of iron are put into the regulus while liquid and left in, so that it may thereby be conveniently lifted out when solid.

Process of smelting.—A single charge for one operation of smelting is 30 ctrs., and is composed of 20 ctrs. of lead-slags, 5 ctrs. of raw, and 5 ctrs. of roasted, ores of Classes C and E. The burnt residue of iron-

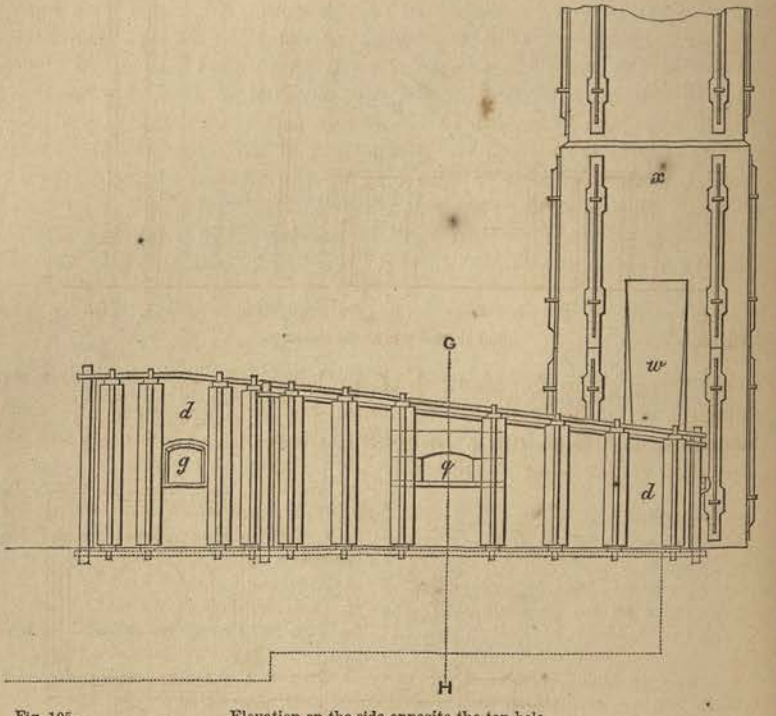

Fig. 105. Elevation on the side opposite the tap-hole.

pyrites, obtained in the manufacture of sulphuric acid, is a good substitute for roasted ore. The slags are first let fall from the hopper into the furnace, and the ore afterwards. On account of deficiency of quartz in the latter, from 1 to 2 ctrs. of quartz are, it is stated, added to each charge.[4] The charge is spread so that most of it may lie near the fire-bridge, in order as far as possible to protect the latter. The working door is closed, and all openings through which air might enter in the body of the furnace are stopped with wet sand;

[4] Vorlesungen, p. 110. My metallurgical friend, Hochstätter, questions the accuracy of this statement respecting the addition of quartz.

the grate is freed from clinker and the fire well kept up; and after the lapse of 2½ hours, the charge with proper firing will be melted and should then be well rabbled. The door is again closed, and a

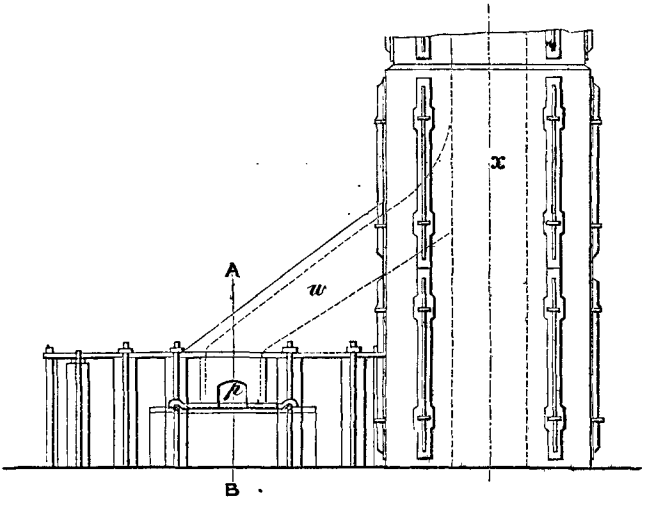

Fig. 106. End elevation near the chimney.

strong firing given for about ¼ of an hour, after which the slag is skimmed off; it flows first into a sand-bed underneath the door and thence into moulds of iron. In order to draw out as much slag as pos-

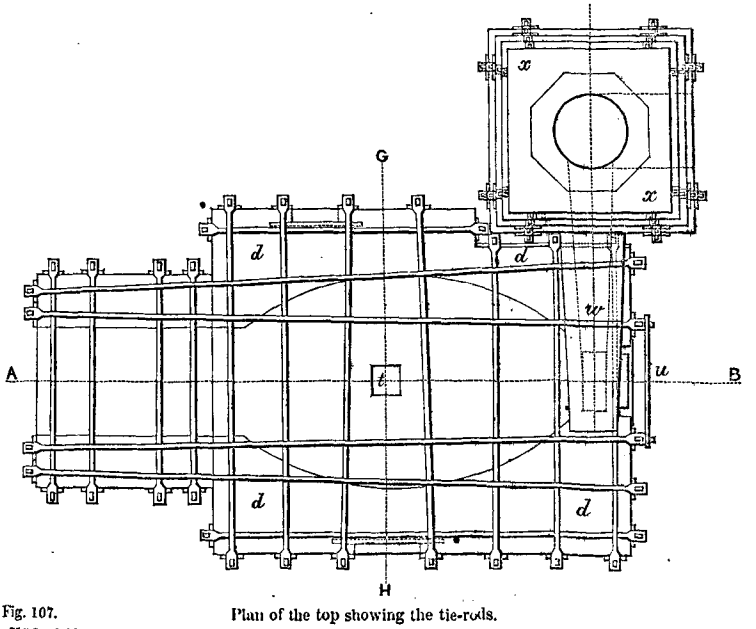

Fig. 107. Plan of the top showing the tie-rods.

sible, a small quantity of the next charge is let fall from the hopper into the furnace, whereby the level of the slag being raised somewhat higher the latter will be forced towards the skimming-door, so as to admit of its more complete withdrawal. After skimming is ended the rest of the next charge is introduced and the process repeated in the manner described. As a rule the regulus is tapped off at the end of the smelting of every third charge into moulds of iron. In the course of 24 hours there are from two to three tappings. When cold the regulus is broken up into pieces about as large as the fist and roasted either in heaps or in suitable calcining-furnaces.

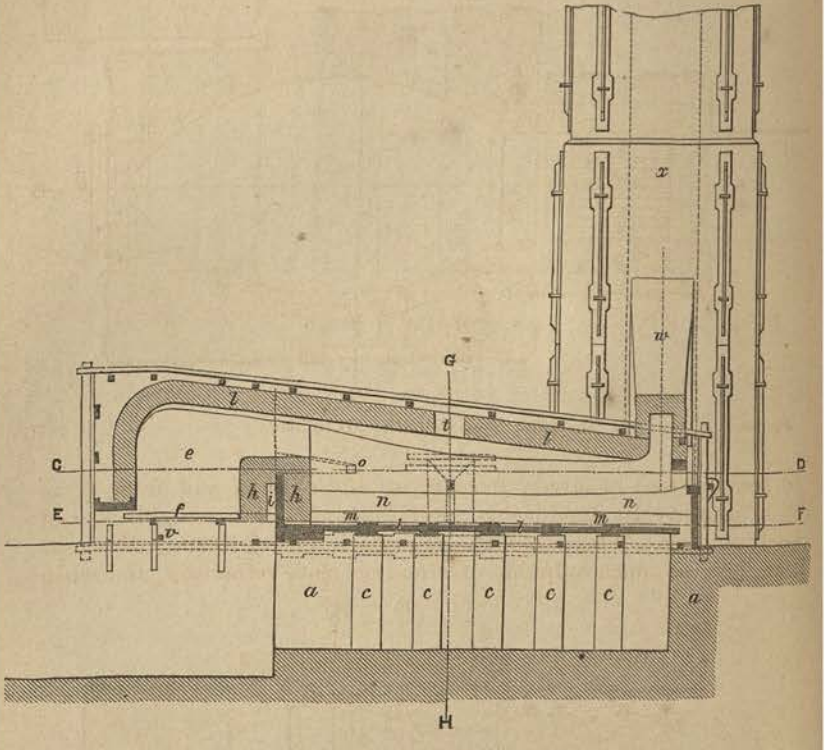

Fig. 108. Vertical section on the line A B, fig. 109.

After each tapping the fire-bridge and bed are repaired where necessary by plastering on a mixture of 5 parts of finely-pounded fire-clay and 2 parts of burnt and coarsely-pounded quartz duly tempered with water.

The consumption of fuel in 24 hours amounts on the average to 60 bushels, or about 114 ctrs. of non-caking bituminous coal.

A furnace roof under the most favourable circumstances lasts from 1½ to 2 years. A smelting campaign continues as long as the bed lasts, which on the average is about a year.

Regulus from slag- and ore-smelting in the reverberatory furnace.—The average production of regulus in 24 hours is about 40 ctrs. This regulus contains from 0·15% to 0·20% (49 ozs. to 65 ozs. 6 dwts.

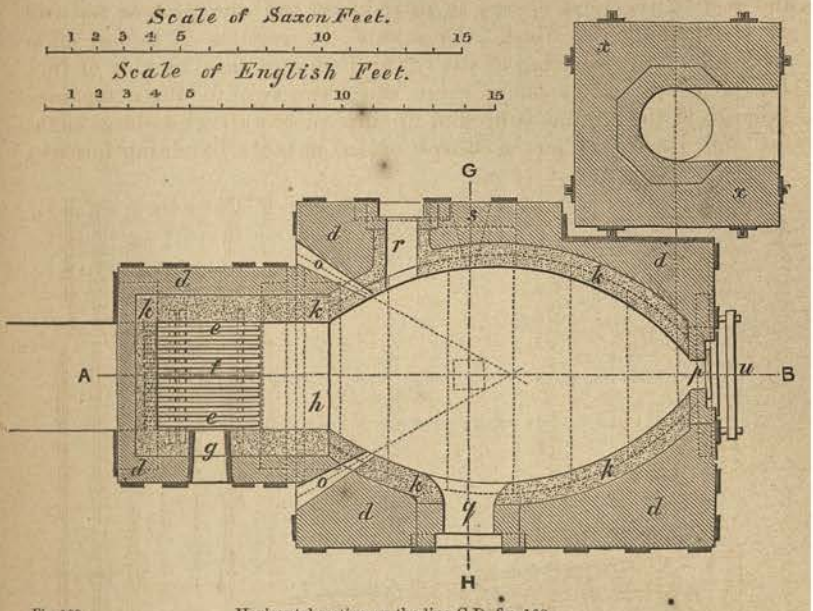

Fig. 109. Horizontal section on the line C D, fig. 108.

16 grs. per ton) of silver, from 8% to 10% of lead, and from 4% to 5% of copper. Its fracture is mostly granular-foliated, black, and feebly shining. When cold the regulus is pretty tough. From its containing so much sulphide of zinc it is more refractory, and when

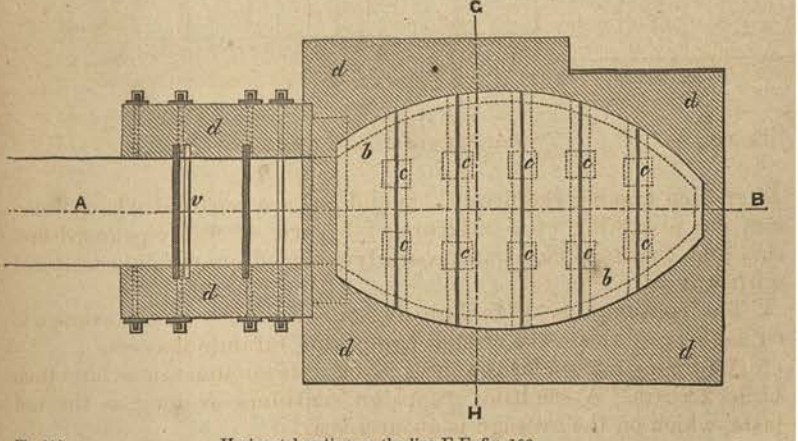

Fig. 110. Horizontal section on the line E F, fig. 108.

liquid less cohesive, and more difficult to roast, because sulphide of zinc oxidizes more slowly than sulphide of iron in the process of roasting. Sulphide of zinc is occasionally present in very considerable quantity, and may often be recognized in translucent particles; and with the aid of a lens, magnetic oxide of iron may not unfrequently be perceived in bright black octahedral crystals in cavities. Often particles of slag may be observed in the regulus, and to such slag is to be ascribed the silica found in analyses of this regulus.

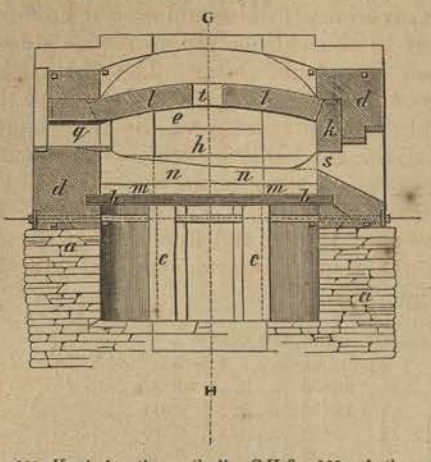

Fig. 111. Vertical section on the line G H. figs. 109 and others.

Composition of Reverberatory Furnace Regulus.

Sulphur	23·43
Lead	7·35
Iron	53·81
Copper	3·87
Zinc	7·65
Arsenic, Antimony	0·84
Silica	2·11
	99·06

Slags from slag- and ore-smelting in the reverberatory furnace.—They are mostly crystalline, feebly lustrous, and in colour vary from greenish to brownish-black. Their specific gravity ranges from 3·70 to 3·86. They contain on an average 1·0% of lead and 0·002% (13 dwts. 2 grs. per ton) of silver. They are used for building purposes or thrown away, only those drawn out towards the completion of the skimming being examined for regulus.

Composition of Reverberatory Furnace Slag.

Silica	36·04
Alumina	5·38
Protoxide of iron	42·60
Lime	6·29
Magnesia, Protoxide of manganese	1·71
Dioxide of copper	0·24
Protoxide of lead	1·34
Oxide of zinc	4·66
Sulphur	1·47
	99·73

From a furnace working well. Analysis by Richter.

An average sample of a large quantity of slags from the Halsbrücke Works. The sulphur in the slag is attributed in part to intermixed regulus, but is also present in combination with calcium.

Experiments with a view to volatilize the zinc in slag- and ore-smelting in the reverberatory furnace.—Such experiments were conducted at Freiberg in 1854. It was conceived that by the addition of sesquioxide of iron and carbon, the metallic iron set free would abstract the sulphur from the sulphide of zinc, with the formation of sulphide of iron and the volatilization of zinc. The following mixture gave the best results, and for convenience of comparison, the usual proportions are stated between brackets:—Lead-slags from ore-smelting in the blast-furnace (20) 24 ctrs., roasted ores of Class E (5) 4 ctrs., unroasted ores of the same class (5) 2 ctrs., fine coke-dust 1½ ctr., and fluor-spar ½ ctr. In another reverberatory furnace the same charge was smelted with the omission of the coke-dust and fluor-spar.

THE REGULUS CONTAINED PER CENT.

	Without coke-dust.	With coke-dust.
Iron	36·55	46·54
Zinc	13·10	4·65
Copper	5·21	6·70
Lead	9·32	7·98

It will be perceived that the addition of carbon prevented much of the zinc from passing into the regulus; but the slags formed in both cases contained a large quantity of oxide of zinc, as will be seen from the following analyses by Richter:—

	I.	II.
Silica	34·30	36·08
Alumina	4·65	3·36
Protoxide of iron	41·96	40·86
Lime	7·45	7·96
Magnesia	1·30	1·01
Protoxide of manganese		0·74
Dioxide of copper	0·15	0·18
Protoxide of lead	0·98	0·73
Oxide of zinc	7·75	6·66
Sulphur	0·80	1·92
	99·34	99·50

I. From the Muldo Works, without coke-dust. II. From the same works, with coke-dust.

The experiments in question were unsuccessful; for, although the regulus produced contained less zinc, yet the smelting was greatly impeded; the consumption of fuel was considerably increased; the slag was thicker and more difficult of separation from the regulus, and required to be re-smelted; and the loss of lead and silver, especially the latter, was sensibly greater. Far better results were obtained in the reverberatory furnace by more completely roasting the zinciferous ores constituting part of the charge.

ACCESSORY PRODUCTS.

Interesting crystallized compounds have been found in breaking up the worn-out sand beds of the reverberatory furnaces at Freiberg, and have been particularly examined by Scheerer and Plattner.

Regulus is infiltrated through the bed, and as it remains there a long time opportunity is presented for its slowly crystallizing under most favourable conditions; and it is subjected in a greater or less degree to the oxidizing action of the free oxygen and aqueous vapour in the gaseous products of the combustion of the fuel passing through the furnace.

Magnetic oxide of iron in small crystals, from $\frac{1}{8}''$ to $\frac{1}{4}''$ broad, is found lining cavities in the infiltrated regulus, mostly in the form of the octahedron and rhombic dodecahedron combined. The crystals composing the thicker lining or crusts are homogeneous throughout, while those of the thinner crust occasionally contain rounded kernels, resembling ordinary regulus and sometimes copper-pyrites, the average proportion of regulus in such crusts amounting to 22·9%. Occasionally minute isolated brass-yellow crystals are found in the infiltrated regulus, which for the most part can only be detected with the aid of a lens: they have been found to have the following composition:—[5]

Sulphur	33·33
Iron	41·65
Copper	20·36
Lead	1·71
Nickel	1·18
Antimony	0·96
Silver	0·09
	99·28

This corresponds to the formula $Cu^2S,FeS+Fe^2S^3,FeS$, or Cu^2S,Fe^2S^3+2FeS, or $Cu^2S+3FeS+FeS^2$.

The formation of the crystals of magnetic oxide of iron, is, as suggested by Scheerer and Plattner, probably due to the action of aqueous vapour upon the infiltrated regulus; and Scheerer makes the interesting remark that chloritic slate at Fahlun contains octahedral crystals of magnetic oxide of iron, which enclose particles of iron-pyrites but oftener of copper-pyrites.[6]

White capillary silver has been found by Scheerer in the bottom of one of these furnaces in a crack near the fire-bridge, as well as in drusy cavities, just as moss-copper occurs in the *blue-metal* of copper-smelters. In other parts of the same crack, where there was no capillary silver, small cubes of sulphide of lead were discovered which were entirely without the usual step-like form of the artificially crystallized sulphide. Here and there upon the sulphide of lead were attached minute crystals scarcely half a line ($\frac{1}{24}''$) broad, and about $\frac{1}{4}''$ long; they belonged to the rhombohedral system; they had a bright metallic lustre and a dark blueish-grey colour; and as they consisted essentially of sulphur and copper, they were regarded as disulphide of copper.[7]

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[5] Allgemeine Hüttenkunde, Plattner, 2. p. 116.

[6] Berg. u. hüttenm. Zeitung, 1855, p. 111.

[7] Ibid. p. 303.

The artificially crystallized sulphide of lead from the beds of these furnaces has been found to contain only small quantities of copper, antimony, and silver.

A foliated, lead-grey product had the following composition :—

Sulphur	17·40
Copper	41·93
Lead	38·60
Iron	0·36
Antimony	0·65
Silver	1·10
	100·04

This corresponds to the formula $9Cu^2S+5PbS$.

Conclusions from the Analytical Data relating to the Freiberg Process.

The analytical data, which have been presented in relation to the Freiberg process of lead-smelting, are incomplete and unsatisfactory. It is true that the composition of the various products obtained in that process has been determined by different chemists at different times; but, so far as I am aware, the average composition of a given smelting-charge,—that is of ores, fluxes and slag,—and of the resulting products has not been ascertained. Now, it may be regarded as certain, that at different times, especially when the intervals are long, as in the case in question, the smelting-charge is not identical in composition; and, consequently, that the analysis of specimens selected under such circumstances will not afford data so precise and consecutive as modern science requires for the explanation of the chemical reactions which occur at each stage of the process. Nevertheless, there is probably sufficient experimental and analytical knowledge of the subject to enable us to establish the theory of this process on a tolerably sure foundation.

The ore-mixture is composed of sulphides and oxidized substances. The principal sulphide, and that which is the chief object of treatment, is argentiferous galena; and the other or subordinate sulphides are iron-pyrites, zinc-blende, and a little copper-pyrites. We may ignore the existence of antimony, arsenic and nickel, as they occur only in very small proportion, and may be practically disregarded. The oxidized substances are protoxide of iron, the so-called earthy bases, lime, magnesia and alumina, sulphate of baryta, fluor-spar, and silica. The problem is the separation of the lead and along with it the silver; and the solution as we have seen, consists in causing the other constituents of the ore to combine and form a fusible slag. Let us suppose that exclusively ore-mixture, such as above-mentioned, is the subject of treatment in the blast-furnace. If the relative proportions of the silica and oxidized substances be theoretically suitable, as may easily be ascertained from data previously given, simple fusion of the raw or uncalcined ore would yield regulus and slag, containing

respectively sulphides and oxidized compounds. If on the other hand, the ore be calcined *sweet* and then smelted in the blast-furnace, the proportion of silica being such as would suffice to form a fusible slag with the oxidized constituents originally existing in the ore and with those generated by calcination, the products would be argento-cupriferous lead and slag containing those constituents except a portion of the copper. As the action of the blast-furnace is deoxidizing, and as oxide of lead is reducible by carbonaceous matter at a comparatively very low temperature, the oxide of lead in the calcined ore would be quickly reduced to the metallic state in descending through such a furnace. But, as in the calcination of galena, sulphate of lead is formed as well as oxide—and indeed in considerably increased proportion when, as in the case supposed, iron-pyrites is present,—that salt would be partially or completely reduced to sulphide of lead, and so a regulus would be obtained along with metallic lead. With respect to the silver, all that needs here be stated is that under the circumstances, it will necessarily be found in the lead; for, assuming the calcined ore to contain sulphate of silver, the whole of the silver would be separated from it in the blast-furnace and be carried down by the lead, as that salt is reduced to the metallic state by heat alone at a temperature far below what prevails in a blast-furnace, and at a comparatively very low temperature when in contact with carbonaceous matter.

From the foregoing considerations, it will be evident, that by a preliminary calcination of the ore, one operation of smelting would suffice for the separation of the lead and silver, with the advantage, it might be shewn, of economy in labour, time, and fuel. But those considerations, it must be borne in mind, are based on theoretically perfect conditions, which cannot be realized in actual practice on the large scale. Nevertheless, the reactions which have been pointed out do occur in practice, and it is only the numerical results that fall short of theoretical perfection. The ore-mixture is, in a chemical sense, far from homogeneous, and the contact of its components with each other cannot be sufficiently prolonged or intimate in a blast-furnace, to ensure such precise and constant results as might be obtained under diametrically opposite conditions in the laboratory on the small scale.

The main principle of the Freiberg process is the oxidation of galena by calcination, and the reduction as completely as practicable in the blast-furnace of the resulting products, namely, protoxide and sulphate of lead; and in order to illustrate that principle in the simplest manner, we have supposed ore alone to be the subject of treatment, and theoretically perfect conditions to be attainable. Now, in actual practice, according to the method described, the lead tapped from the blast-furnace is impure, the regulus contains a large proportion of lead and iron, with some zinc, copper and other metals, and the slag retains a notable proportion of lead, existing partly as silicate and partly as metal and regulus mechanically diffused. The proportions of lead both in the regulus and the slag are too large to be

neglected; and, consequently, it is necessary to subject each of those products to further treatment with a view to extract as much of the lead contained in them as possible, consistently with economy.

It has been stated that the actual smelting-mixture at Freiberg is composed of ores, slag from former smelting-operations in the same furnace, and regulus from slag- and ore-smelting in the reverberatory furnace; and it may be asked, why should this be done? The regulus is previously calcined and the product may be regarded as substantially composed of oxide of iron, about 7% of lead in the state of protoxide and sulphate, and oxides of zinc, copper, &c. Assuming sufficient silica to be present in the smelting-mixture, the oxidized products of lead in the calcined regulus are for the most part reduced in the blast-furnace, and the oxide of iron passes into the slag forming silicate of protoxide along with any oxide of lead, zinc, copper, &c., which may escape reduction. Any zinc, which may be reduced from its oxide will be volatilized, being partly evolved from the mouth of the furnace and partly re-oxidized and deposited as an incrustation round the throat; and should any of the reduced metal in its ascent come in contact with sulphide of lead or copper, that sulphide would in a greater or less degree be reduced with the formation of sulphide of zinc. The calcined regulus may be practically viewed as calcined ore free from so-called earthy matter and silica; and its constituents undergo in the blast-furnace, in the presence of the necessary proportion of silica, precisely the same chemical changes as the similar constituents of the calcined ore-mixture.

It may be asked why any slag from the blast-furnace, which is the special subject of treatment in the reverberatory furnace with the object of extracting as far as is practicable with economy the lead which it contains, should be re-smelted in the blast-furnace along with ore and calcined regulus from the reverberatory furnace? Now, it is evident that as the slag produced in the blast-furnace has the same composition as the slag added, the action of the latter cannot be chemical, and would, therefore, seem to be essentially mechanical. By addition of such slag, the nose is more quickly formed and more easily maintained and regulated than when only uncombined slag-forming ingredients are used; the furnace is less liable to "gobbing," and its lining is more or less protected from direct contact with *uncombined* metallic oxides, especially that of iron, of which the action is highly corrosive. Again: if the slag added contain a notable quantity of intermingled regulus and shots of metals, these would be more or less completely separated.

The principles, which have been enunciated with respect to ore-smelting in the blast-furnace, will in great measure apply to the smelting of the regulus from that furnace. The regulus is calcined and smelted in conjunction with coppery ores, slag rich in oxide of lead, which is formed in the reduction of litharge (see description of this reduction in a subsequent part of this volume), slags which accompanied the formation of this regulus, and fluor-spar. The lead in the oxidized products in this mixture is for the most part set free

and trickles down into the hearth; and a second regulus is produced, which contains much more copper and less iron than the original regulus. Most of the iron in the smelting-mixture passes into the slag, which approximates in composition to tribasic silicate of protoxide of iron, while most of the copper passes into the second regulus. This will be understood, when it is recollected that in any mixture containing copper, iron, oxygen, sulphur in the state of sulphide, and silica, whatsoever may be the proximate constitution of such mixture, the copper will be separated as regulus, provided that somewhat more sulphur is present in the state of sulphide than suffices to form disulphide of copper, and the relative proportions of the iron, oxygen and silica are such as may give rise to the formation of tribasic silicate of protoxide of iron. The following reaction may also come into play. The metallic copper, which may result from the reduction of oxide of copper by carbonaceous matter in the blast-furnace, will decompose any sulphide of lead with which it may come in contact, with the formation of disulphide of copper, containing a little sulphide of lead, and metallic lead containing a little copper. In this manner enriched copper-regulus is obtained, and by again calcining such regulus and smelting the product as in the first instance, lead, and another regulus still richer in copper than the last, will be separated; and so this treatment may be repeated until a regulus is formed, containing about 70% of copper.

In smelting the slag from the blast-furnace in conjunction with raw and calcined pyritic ores of the classes C, E, two products are formed, regulus containing as much of the lead as can practically be extracted, and slag approximating in composition to tribasic silicate of protoxide of iron and retaining a little lead, which cannot be profitably separated. There is present *much more* sulphur in the state of sulphide, chiefly that of iron, than suffices to form sulphide of lead, and sufficient silica to combine with all the iron and produce tribasic silicate of protoxide. A regulus is, therefore, produced containing the lead, a large quantity of sulphide of iron, and sulphides of zinc, copper, &c. The large proportion of sulphur, beyond what is required to combine with the lead, causes the separation of the latter metal as far as practicable, and increases the fusibility of the regulus by the addition of readily fusible sulphides, without which sulphide of zinc might be present in sufficient proportion to render the regulus very refractory. The inconvenience occasioned by zinc-blende in lead-smelting will be hereafter considered in the description of the Przibram process.

Yields and Loss.

In the second half of the year 1862, the following results were obtained in the smelting of lead-slags, the total quantity of which amounted to 4897·05 tonnes (metrical tons):—

Materials smelted.	Tonnes.	Percentage of Silver.	Percentage of Copper.	Total Lead. Tonnes.	Total Silver. Kilogrammes.	Total Copper. Tonnes.
Slags	4897·05	0·000507	..	240·53	1422·00	19·74
Ores { Class C ...	2257·18	0·0505	..			
Ores { Class D ...	144·98	0·0456	1·100	..	1655·92	2·30
Ores { Class E ...	2854·15	0·0156	0·007			
					3077·92	22·04
Regulus produced	2320·00	..	..	112·15	3034·00	46·40
Slag thrown away	7957·00	..	..	120·85	40·34	..
				233·00	3074·34	46·40
				Loss. 7·53	Loss. 3·58	Increase. 24·36

Carnot remarks, doubtless correctly, that the quantity of metal in the ores notably exceeds that stated in the assay books of the Freiberg Smelting Works. A considerable excess of copper might be expected; but the excess obtained is equal to the weight of copper stated in those books, which proves either that the method of assaying copper ores or copper products practised at Freiberg is very inaccurate, or that cupriferous matters were smelted in which the proportion of copper was not ascertained. Dry methods of assaying either poor lead ores or poor copper ores are very unsatisfactory.

There is certainly considerable loss both of lead and silver, particularly of lead; but Carnot found it impossible to procure data on that head, even approximately correct. He estimates the loss of silver at 1·11% of the total silver, and the loss of lead at 19·27% of the total lead. "These losses," he writes, "are only the *apparent* losses. The *real* losses are unknown, and assuredly much greater; but thanks to the mode of purchase of the ore, the excess which they present over the apparent losses is left to the charge of the mines, since in the purchase no account is taken either of the losses by assay or even of the metals below a certain minimum proportion." It is far better that the exact quantities of the metals in ores or other matters subjected to metallurgical treatment should be accurately known than that a system of guess-work, based on the confessedly inaccurate reports of assayers, should be tolerated. Let the loss, however large, be known; for such knowledge, especially if the loss be large, will be a powerful stimulus to excite strenuous and persevering efforts towards its diminution.

According to Von Beust, the loss in 1865 was 1% of silver and 15% of lead. In former times it was much greater, and, according to the accounts for the period of ten years, from 1761 to 1770, amounted to 4% on the silver and 81·5% on the lead. This enormous loss of lead is attributed to the imperfect construction of the furnaces, and the improper relation of lead to silver in the charge. The lead was in fact regarded mainly as a convenient agent

for bringing out the silver, rather than as a material having a value of its own.[8]

Smelting Costs.

Carnot seems to have been at great pains to obtain information on this subject, and has published the following statements thereon.

Ore-smelting in the blast-furnace.—The cost during the second half of the year 1862 is estimated per ton of 1000 kil. of material smelted, which may practically be taken as the same as the English ton.

		Francs.
Labour	Smelters and superintendent, 1·778 day	3·415
	Regulus roasters, 0·136 day, at 1 f. 20	0·204
	Wheelers, 0·612 day, at 1 f. 20	0·734
Fuel	Coke, 0·310 ton, and wood-charcoal 0·36 kil.	7·075
	Coal for roasting regulus, 0·019 ton	0·222
Fluxes, 0·003 ton of fluor-spar, at 17 f. 70		0·053
Blast and stamps		0·566
Maintenance of furnaces and tools		0·891
		13·160

s.	d.
10	6

Slag- and ore-smelting in the reverberatory furnace.—During the second half of the year 1862, cost per ton of materials smelted:—

		Francs.
Labour	Smelters, Labourers	2·066
	Accessory work	0·244
Fuel	Coal, Liguite	7·572
Maintenance of furnace and tools		1·298
		11·180

	s.	d.
About	8	11

Smelting in the reverberatory furnace of slags from regulus-smelting: cost per ton of regulus from the blast-furnace, inclusive of the cost of roasting the ores added:—

	Francs.
Labour	6·220
Fuel (1·589 ton)	22·195
Maintenance of furnaces and tools	2·932
	31·347

	£.	s.	d.
About	1	5	1
Add	1	7	1
Total	2	12	2

[8] Festschrift zum 100-jährigen Jubiläum der K. S. Berg-Academie zu Freiberg, p. 327.

Regulus-smelting.—During the second half of 1862. In the blast-furnace, inclusive of cost of roasting ores and reguluses, per ton of regulus from the blast-furnace:—

		Francs.
Labour		8·820
Fuel	Coal	3·065
	Wood	0·156
	Coke	16·678
Fluxes	Fluor-spar	0·640
	Sulphate of baryta	0·064
Stamps		1·179
Blast		0·686
Maintenance of furnaces and tools		2·579
		33·867

	£.	s.	d.
About	1	7	1

Treatment of Copper-Regulus.

The subject of this treatment is the copper-regulus (*Spurstein*) described at p. 317, and the object is the extraction of the copper and silver from that regulus, which may be attained in two ways. In either case the regulus is first roasted and smelted, whereby a much richer regulus is produced containing, say, 70% or more of copper, and some rich argentiferous lead is at the same time separated. The last regulus is then desilverized by Augustin's method (to be fully considered in the next volume) and afterwards smelted for metallic copper in the usual manner;[9] or it may be applied to the manufacture of sulphate of copper or blue-vitriol,[10] and to Reich, of Freiberg, is due the credit of having first carried it out in practice to a successful issue. In the former method the regulus should, as far as possible, be deprived of lead; but in the latter, the presence of lead is advantageous to the collection of the silver; there should, however, in this case be as little iron as possible in the regulus. Carnot asserts the contrary with respect to the presence of lead; and he obtained his information at Freiberg.

The regulus is for the most part roasted, but some is used raw or unroasted. Flat-bottomed reverberatory calciners are employed in the process of roasting, indeed, the same double-bedded furnaces as mentioned in the foregoing description of lead-smelting at Freiberg. The regulus is previously stamped and reduced to fine powder.

Smelting takes place in the same kind of reverberatory furnace as that adopted in slag- and ore-smelting. A charge consists of from 18 to 25 ctrs. of regulus at the most, of which by far the greater part[11] is roasted, and of from 10 to 12 ctrs. of sulphate of baryta and quartz, the latter constituting from $\frac{1}{2}$ to $\frac{2}{3}$ of the mixture; occasionally barytic

[9] See the 1st volume of this work.

[10] Such is the statement in Plattner's Allgemeine Hüttenkunde, published at Freiberg in 1863; but, according to Carnot, whose previously quoted paper was published in 1864, Augustin's process was abandoned in 1860, and only the other process was in operation when he wrote.

[11] According to Hochstätter, $\frac{3}{4}$.

slags from this same smelting are substituted in part for those fluxes. When the regulus is to be applied to the manufacture of blue-vitriol, about half a bushel (about 1½ English bushel) of fine coal-slack is added to the charge, with the object, it is stated, of reducing any oxide of lead which may have passed into the slag. From 6 to 7 charges are smelted in 24 hours. The enriched regulus contains from 68% to 75% of copper, 3% to 8% of lead, and 0·3% to 5% of iron.

A regulus of this kind was found by Reich to have the following composition :[12]—

COMPOSITION OF ENRICHED REGULUS.

Sulphur	20·05
Copper	70·75
Lead	5·35
Iron	1·55
Nickel	0·70
Arsenic with a little antimony	1·35
	99·75

[*Note by Richter.*—At the present time (1868) this regulus contains from 72% to 73% of copper, and never more than 0·3% of iron.]

The slags are pretty fusible, of a dark colour and glassy lustre; and notwithstanding their high specific gravity,[1] which is due to the presence of a considerable quantity of baryta, they allow of a very complete separation of the regulus: they hold from 1% to 3% of copper.

The function of sulphate of baryta in this process is not so evident as has been stated. There is no doubt that without the use of this substance, an equally rich regulus would be obtained in the copper works at Swansea, accompanied with an equally clean, if not cleaner, slag. Plattner gives the following explanation of the action of sulphate of baryta. "Its application is founded on its easy decomposability in admixture with silica and sulphide of iron. The resulting protoxide of iron forms with baryta and silica a very easily fusible slag, while the sulphide of barium produced at the same time exerts a sulphurizing effect on the oxidized copper. If the proportion of roasted to unroasted regulus be very large, part of the sulphate of baryta may be replaced by barytic slags, which then act chiefly as a flux."[2]

According to Carnot, the coal is added in order to reduce the sulphate of baryta to sulphide of barium, and not to reduce oxide of lead in the slag, as previously stated.[3] Sulphate of baryta is completely reduced by carbon at a comparatively low temperature, with the

[12] Carnot, op. cit., p. 123.
[1] Plattner, op. cit., p. 196.
[2] Op. cit., p. 196.
[3] Many years ago I saw carbonic acid produced on this principle, and applied to the manufacture of white-lead, at the chemical works of Mr. Sewell, at Nottingham. A mixture of sulphate of baryta and coke-dust was heated in iron retorts, precisely similar to those used at gas-works. The sulphide of barium was thrown away into the river Trent hard by. The process was patented.

formation of carbonic acid. In this process much of the lead is volatilized, and the rest passes partly into the enriched regulus and partly separates in the metallic state, carrying with it silver; and generally a little black-copper is formed, which is easily removed in the subsequent operation of stamping the regulus, it being so malleable as to be only flattened out and not pulverized under the stamps. The black-copper thus extracted is converted into regulus by fusion along with copper-reguluses.

Treatment of enriched regulus in the manufacture of blue-vitriol.—It should not contain more than 0·3% of iron at the most. It is stamped and sifted, and roasted *sweet* in a reverberatory calciner. The operation is divided into two stages, *fore-roasting* and *sweet-roasting*. In the first stage 8 ctrs. of regulus are roasted during 8 hours, and the product is then ground and roasted during 4 hours more. The temperature, it is scarcely necessary to remark, should be carefully regulated so as to prevent clotting, and towards the end, according to the information received by Carnot, should be sufficient to decompose any sulphate of silver which may have been formed, and which requires a higher temperature for its decomposition than either sulphate of iron or even sulphate of copper. Any clotted lumps which may have been produced are stamped and again roasted for 1 or 1¼ hour.

Solution.—The roasted regulus is next exposed to the solvent action of hot sulphuric acid—the so-called "brown oil," as it comes from the leaden chambers (*Kammersäure*), having a specific gravity of from 1·494 to 1·525 (Carnot says 1·380) and diluted with its own bulk of water or of mother-liquor produced in a subsequent stage of the process. Solution is effected in cylindrical wooden tubs lined with thick sheet-lead, about 4′ deep and 2′ 7″ in diameter, inside measure. A leaden pipe about 1¼″ in diameter descends to the bottom of each tub for the introduction of superheated steam. There are two rows of such tubs arranged one higher than the other for the convenience of manipulation. Each tub is charged with 4 ctrs. of brown oil diluted as above stated, steam is let on, and 2 ctrs. of prepared roasted regulus are added in small portions successively, stirring being kept up continually. The regulus is conveyed in iron boxes, each containing the proper measure, and so the trouble of weighing is avoided. From time to time water or mother-liquor is added in order to dissolve the anhydrous sulphate of copper separating; but only so much as suffices to maintain the specific gravity between 1·380 and 1.4707. Solution is completed in about 4 or 5 hours, when the steam is shut off. The whole is left at rest for about an hour, in order that the suspended matter may settle to the bottom, and the supernatant liquor is then drawn off by a leaden syphon into a settling or clarifying vat. The residue is covered with water to the height of about 6″, the steam is again let on, and a tap in the bottom of the tub opened, when the muddy contents flow into a vessel, from which the solid deposit that forms therein is taken out and dried. This deposit amounts to about $\frac{1}{10}$ of the weight of the regulus, and should contain the whole of the lead and silver of the regulus, together with some oxide iron

and copper, which experience has shown it is more economical to leave in that residue than to dissolve out completely.

Crystallization.[4]—From the settling-vats the solution is drawn off into crystallizing-tanks, which are of wood, lined internally with sheets of lead soldered together, 7′ 8″ long, 4′ wide, and from about 2′ to 2′ 9″ deep, inside measure. Pieces of wood are placed at intervals across the tanks, resting on the edges of the latter, and upon them are hung numerous small plates of lead, which plunge some inches into the solution underneath. On these plates crystals of sulphate of copper begin to form, and continue to grow into bunches. The solution is left 7 or 8 days in the tanks; its specific gravity at first is 1·435, and 1·1981 or 1·2080 after the formation of the crystals.

The crystals of crude vitriol (A) are redissolved in water or in vitriolic liquor with the aid of a steam-jet, and the solution resulting, which has a specific gravity of from 1·260 to 1·283, is crystallized after the deposition in another vessel of the finely-suspended matter which it contained. The products are, 1st, Crystals of good vitriol, which are washed upon a sieve during a few seconds, then drained upon inclined tables, and afterwards spread out on drying-boards. In this operation of washing some fine or small vitriol is separated, which, though pure, is not marketable, and is therefore redissolved along with crude vitriol and crystallized afresh; 2nd. Small crystals less pure than the last, formed at the bottom of the solution, and termed bottom-vitriol, which are also treated anew along with the crude vitriol; 3rd. Mother-liquor (B) which goes back to the solution of crude vitriol.

The new liquor is less pure and weaker than the first; but three products are got from it corresponding to those above described, namely, marketable vitriol, bottom-vitriol, and mother-liquor, which last is employed in the same way as that preceding until it becomes too weak, when it is evaporated in leaden basins, heated cautiously by a fire underneath, until its specific gravity is raised to about 1·283. The concentrated hot solution is transferred to the crystallizing tanks, and there yields marketable vitriol, and mother-liquor, which is poured in portions upon the poor roasted ore, and of which, consequently, the contents enter into the general treatment in the operation of slag-smelting.

The mother-liquor (B) of the first crystallization, is used along with fresh sulphuric acid for dissolving roasted regulus: the solution by evaporation yields crystals of crude vitriol, which are treated like the first or even along with them, and the mother-liquor is used again for dissolving regulus. This course is repeated three or four times, the mother-liquor always being reserved for solution of fresh regulus; at last it is evaporated until it acquires a specific gravity of 1·435 when it is set to crystallize, crude vitriol being obtained and

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[4] Carnot, op. cit., p. 127, from which much of the preceding, as well as much of the following, description is taken. I have adhered as far as I have thought necessary to the language of Carnot. There is much more detail in Carnot's account than in that of Plattner; but in essential points the two accounts agree.

mother-liquor charged with iron, which is also poured upon the roasted ores while hot; or the copper which it contains may be precipitated by iron.

The process is carried on in the building formerly devoted to the well-known Freiberg Amalgamation Works. There are 8 dissolving-vats, 8 settling-vats, 52 crystallizing-tanks, 3 flat evaporating-basins, a place of deposit for the residues, a drying hearth, 6 large vitriol dryers, and 19 other vessels for divers purposes. In order to raise the liquors from the lower to the upper vessels the following apparatus is adopted. The solution is transferred to a vertical cylinder lined with lead, capable of being perfectly closed, and forced up by the admission of compressed air at the top.

Economical results.[5]—During a campaign of 6 months in 1862, 103·765 metrical tons of enriched regulus, containing 70% of copper, and about 130¾ ozs. of silver per ton, were operated upon, together with 0·430 ton of coppery products (*crasses*), containing 60% of copper and about 311¾ ozs. of silver per ton. Purified sulphuric acid,[6] free from arsenic, was used, which amounted to 204·830 tons, containing 116·540 tons of the specific gravity 1·834. The products were 246·275 tons of crystallized sulphate of copper, containing 25·4% of copper, and 22·810 tons of residues, containing about 30% of lead, from 4% to 18% of copper, and from about 424¾ to 751¼ ozs. of silver per ton. By assay a loss of 4·34% of the total silver present and 3·52% of the total copper was indicated.

Observations.—I have had occasion to conduct experiments on a large scale, in which extremely rich argentiferous disulphide of copper was ground under edge-stones, sifted fine, roasted sweet, and dissolved in diluted sulphuric acid heated by high-pressure steam. The solution of sulphate of copper was evaporated in a circular vessel of lead (heated underneath), and crystallized. The crystals were found to contain a notable quantity of sulphate of protoxide of iron, from which they were not freed by simple recrystallization. However, on peroxidizing the iron and afterwards evaporating, crystals were produced free from iron. Iron in the state of peroxide may be quickly and completely thrown down by boiling with an equivalent proportion of protoxide of copper.

I do not see the reason for Carnot's insisting that the temperature towards the end of the roasting of the regulus should suffice to decompose any sulphate of silver which may have been formed; for nothing would be simpler and easier than to precipitate by metallic copper any silver which might be dissolved along with sulphate of copper.

Produce of the Freiberg Mines in 1867.

In the year 1867 the Freiberg mines produced 31,057½ tons[7] of ores, containing 64,949·3 lbs. of silver, 4663⅝ tons of lead, 71·15 tons

[5] Carnot, op. cit., p. 132.

[6] By passing through it sulphuretted hydrogen, which precipitates arsenic as sulphide.

[7] Metrical tons. 1 ton = 1000 kilogr.; 1 lb. = 0·5 kilogr.

of copper, 604·13 tons of zinc, 158·55 tons of arsenic, 1208·8 tons of sulphur, and 12 lbs. of nickel and cobalt, the money value being 1,858,516·3 thalers, or 278,777*l.* 10*s.*

LEAD-SMELTING AT PONTGIBAUD.

The production of lead in France is comparatively insignificant, and there is no French process of smelting lead that may be regarded as either typical or particularly worthy of imitation.[1] Thus Rivot, professor of the École des Mines in Paris, remarks, "the various works [lead-smelting works of France] follow different methods, which are determined by the nature of the ores or by local conditions, or which only proceed from an imitation more or less complete of the processes adopted in other countries."[2] The works of which he gives the names, and which therefore, it may be presumed, he considered the most important, are those of Vialas in the department of the Lozère, in the South of France; Pontgibaud in Auvergne, dep. of Puy-de-Dôme; Poullaouen in Brittany;[3] Biache, near Arras, dep. of Pas-de-Calais; and Marseilles. I have selected for description the works at Pontgibaud, because Rivot has particularly investigated the metallurgical reactions of the process formerly carried on there, and has published analytical results of general interest. Not long after the completion of that investigation, the mines and smelting establishment came under the management of English mining engineers, Messrs. Taylor, who, I am informed, changed the method of smelting, though not with the advantage at first anticipated. Rivot and Zeppenfeld made a joint communication on the subject to the Annales des

[1] Rivot prefaces his description of the treatment of Argentiferous Galena in England with the following remarks: "Presque toutes les usines achètent les minérais et doivent leurs bénéfices à l'habileté commerciale de leurs directeurs, bien plus encore qu'à la perfection du traitement métallurgique." (Principes Généraux, p. 316.) "Nearly all the works buy their ores, and owe their success much more to the commercial skill of their directors than to perfection in the metallurgical treatment." There are managers in British lead works who thoroughly understand both the science and the practice of their art; and the metallurgical results obtained in those works are, on the whole, quite as satisfactory as any obtained in lead works on the Continent, not even excepting France.

Burat makes the following somewhat disparaging remarks concerning French mining enterprise:—"The 'massif' of the Vosges is, of all the metalliferous districts of France, that which would present most chances in the re-opening of former workings. The lodes of argentiferous lead, at once numerous and strong, there form the chief feature of metallic wealth. Those lodes, opened from time immemorial, still yielded considerable produce in the course of the last century: they are now nearly all abandoned on account of the invasion of water, and could not again be worked without a pretty large outlay. If, when the facility of the first exploitations yielded large profits, part of those profits had been expended every year in preparation for future work, the continuance of the mines would have been assured, whereas at present almost all the exploitations in France no longer exist except to accuse the past. Suppose this district of the Vosges in the hands of the population of the Harz or of Saxony, and without any doubt it would then have been maintained in exploitation; for their own metalliferous lodes are only rendered valuable by intelligent management, which has sustained them during centuries."—Géologie Appliquée. Par M. Amédée Burat, Ingénieur, Professeur d'Exploitation des Mines à l'Ecole Centrale des Arts et Manufactures, etc.; p. 168.

[2] Principes Généraux du Traitement des Minérais Métalliques. 1860. 2. p. 570.

[3] Long since closed.

Mines, which afterwards appeared as a separate volume in 1851;[4] and yet in his general treatise on the Metallurgy of Lead and Silver, published in 1860, he scarcely notices Pontgibaud, while he describes at length the smelting works at Vialas, which he represents as situated in a very disadvantageous locality, especially with respect to fuel, and which, as far as I can perceive, exhibit no particular feature of interest. Although another process may have been substituted at Pontgibaud for that which was in operation there when Rivot wrote, yet in the following account of it I shall use the present tense.

The town of Pontgibaud is 23 kilometres (14·3 miles) distant from Clermont on the road to Limoges, and in its environs are the mines. The ore is galena, and the rocks in which the metalliferous veins occur chiefly consist of slates, gneiss, and granite, traversed by dykes of porphyry and covered here and there with layers of basalt, volcanic ashes, and flows of lava from the neighbouring Puys. In the working of several veins great difficulty has to be encountered from the copious evolution of carbonic acid. The vein-stuff in one vein only is entirely quartz, while in the other veins it is felspathic and differs but slightly from the incasing granite. Some veins contain sulphate of baryta, not however below the depth of 80 metres (about 87½ yards), whereas the quantity of quartz seems to increase with the depth. The galena, which is always argentiferous, occurs granular or steel-grained, lamellar, well crystallized, most frequently in small dodecahedrons, nearly always bright; but sometimes dull and black, a variety which has often been found very rich in silver, rarely in parallel bands, but generally disseminated in strings or irregular spots, and often penetrating the walls in little strings or isolated spots. The proportion of silver in the ore is pretty high, but varies much in different parts of the lodes: the ore-furnace lead usually contains from 300 to 500 grammes per 100 kilogrammes (98 to 163 ozs. per ton, nearly). The galena is frequently accompanied by a little zinc-blende and spots of iron-pyrites, and more seldom by a little grey copper ore in certain veins of galena, very rich in silver, on the side of Vernède, where fluor-spar is the vein-stuff.

The ores being comparatively poor in lead, though rich in silver, are for the most part subjected to mechanical treatment; but the dressing of them for lead cannot be carried very far, because the stuff thereby separated and thrown away as waste contains a sensible proportion of silver. The limit, therefore, of their enrichment by this means is determined by the capability of their subsequent metallurgical treatment with advantage. They are chiefly in the state of coarse ore or even of slimes when prepared for smelting. Moreover, fuel is dear, and this dearness combined with the poorness of the ore

[4] Description des Gîtes Métallifères, de la Préparation Mécanique et du Traitement Métallurgique des Minérais de Plomb argentifères de Pontgibaud. Par M. Rivot, Ingénieur des Mines, et M. Zeppenfeld, ancien élève de l'Ecole des Mineurs de Saint-Etienne. Paris, 1851. In the following account I have derived my information from that source; and I shall translate literally wherever I consider it expedient to do so.

in lead and other circumstances dependent on locality, necessitates, it is affirmed, the particular method of smelting adopted. Treatment in the reverberatory furnace is considered inapplicable on account of the feeble produce of lead and the large quantity of siliceous matter in the dressed ore; and, on the other hand, the powdery condition of the ore prevents its being directly smelted in the blast-furnace. The process comprises two operations:—1st, Roasting in the usual manner, and then raising the temperature high enough to cause the product to soften and agglomerate into lumps; and 2ndly, Smelting these lumps in a blast-furnace.

Roasting and agglomerating-furnace.—It should rather be described as two furnaces than as one furnace with two beds at different levels, and, accordingly, I shall so describe it. One furnace (A) is constructed like an ordinary reverberatory furnace intended for smelting, and in this the agglomeration of the roasted ore is effected. The grate is $1^m\,20$ (3′ 11·57″) wide by $0^m\,75$ (2′ 5·53″), and $0^m\,75$ (2′ 5·53″) below the top of the fire-bridge, which is $1^m\,20$ wide (3′ 11·57″) and $0^m\,20$ thick (7·87″) and is traversed by a channel of cast-iron for the circulation of cold air through it. The bed is 2^m long (6′ 6·74″) and $1^m\,60$ wide (5′ 3·32″). The bottom is of fire-brick covered with a layer of lime and sand $0^m\,10$ thick (3·94″), and it inclines slightly towards the doors. There are two doors, both on the same side, close together. Rivot mentions only two doors, but a third door is shown in his engraving at the end where the roasted ore falls down, and such a door seems needed here. The other furnace (B) is placed 3^m (9′ 10·11″) higher than A in a continuous line, and is a flat-bedded calciner $10^m\,12$ long (33′ 2·43″) and $1^m\,80$ wide (5′ 10·87″); the height of the roof from the bed is $0^m\,45$ (1′ 5·72″): there are seven doors on each side at equal intervals. The configuration of the ground is such as to admit of this arrangement of one furnace above the other. One end of B communicates with A at the end furthest from the fire-place by a vertical flue, and the other end of B is connected with a high stack by intermediate condensation-chambers, and an underground flue in which the draught is promoted by a fan. There is also a short special chimney, independent of the main stack, which may be used when necessary, suitable dampers being provided for the purpose. The furnace B is made of common brick. It will be perceived that the furnace B is heated by the gaseous products of combustion from A, that the temperature of A much exceeds that of B, and that the ore roasted in B may be easily transferred to A.

Method of proceeding.—The ore is introduced from a hopper into B through a hole in the roof near the stack end, and is gradually advanced towards the opposite end, when it is let fall into the furnace A underneath, where, being exposed to a much higher temperature, it is agglomerated. Four men are required at a time to attend to B and two to A: a shift lasts 8 hours. The temperature of A is kept constantly at bright redness, while in B it is dull red near the flue connecting it with A, and decreases to about 235° C. at the other end. Usually about $7\frac{1}{2}$ metrical tons of ore are passed through these two fur-

naces in 24 hours in 10 or 11 charges: the furnace B contains 6 charges at a time. The roasting should be conducted with much care, so as to oxidize the sulphides as far as practicable. The ore reaches the end of the bed near A in about 12 hours after its introduction. The roasted product after it has fallen into A agglomerates and quickly melts on the surface; it should be continually rabbled, and the melted mass withdrawn through the door nearest the fire, but only when the lower portions have become so stiff that the rabble can no longer be worked. The molten product thus taken out should coalesce into a single cake, weighing about 300 kilogrammes (661½ lbs.), which should be immediately cooled with water. In the operations of roasting and agglomerating, the ore loses from 11% to 12% of its weight.

The agglomerated cakes are dull and almost black on the surface, and it is difficult to determine from inspection whether oxidation has been carried far enough; but after they are broken into pieces as large as the fist, the fracture readily indicates whether the process has been properly conducted: it should be greenish-brown, almost black, have a glassy lustre and porphyritic structure, due to the presence of numerous uncombined particles of quartz or sulphate of baryta, just as in the common ore-furnace slag of the Swansea copper-works. If the temperature has been too low and fusion imperfect, the product on fracture is vesicular, dull, and presents small shining plates of sulphide of lead.

COMPOSITION OF ROASTED AND AGGLOMERATED ORE.

		I.	II.
	Oxide of zinc	0·6	0·7
	Oxide of lead	1·5	3·4
	Oxide of iron	0·7	3·1
	Sulphate of baryta	7·4	7·2
	Sulphate of lead	6·7	7·1
	Sulphide of lead	1·4	5·7
	Silica, quartz, and felspar	24·1	16·5
	Oxide of lead	34·1	37·2
In the state of silicates.	Oxide of zinc	3·3	3·4
	Protoxide of iron	16·3	11·0
	Magnesia, alkalies	1·3	1·5
	Lime and baryta	1·0	1·1
	Arsenic and antimony	traces	traces
		98·4	97·9
	Total metallic lead	37·0	39·0

I. Glassy and porphyritic, no galena was visible. II. Vesicular, but no galena was visible.

RESULTS OF DRY ASSAYS.

		I.	II.
For 100 kil. of ore	Lead	35 kil.	36·20 kil.
,,	Silver	122 gram.	127 gram.
For 100 kil. of lead	Silver	349 gram.	360 gram.
Per ton of lead, about	Silver	114 ozs.	117½ ozs.

COMPOSITION OF THE ROASTED, BUT UNAGGLOMERATED ORE.

Oxide of lead	29·7
Oxide of zinc	3·0
Oxide of iron	15·0
Sulphate of lead	9·5
Sulphate of iron	3·2
Sulphate of zinc	1·5
Sulphate of baryta	8·0
Sulphide of lead	3·2
Quartz and felspar	25·0
Arsenic and antimony	0·4
	98·5

The roasted ore, which was the subject of this analysis, was the same as that from which the specimens of agglomerated product referred to in the preceding analysis were derived, so that the effect of the agglomerating process may be approximately deduced from the composition of the ore immediately before it was subjected to that process and afterwards. Rivot remarks, "that it is doubtless impossible to found a rigorous comparison on the results of analysis of these different specimens, which should not exactly represent the composition of the oxidized and agglomerated ores. But it may be inferred from the greater proportion of sulphates contained in the oxidized [simply roasted] specimen, that the period of agglomeration has for its result the expulsion of a certain quantity of sulphuric acid formed in the roasting properly so called. One may assure one's self, moreover, in following attentively the period of agglomeration, that a certain quantity of sulphurous acid is disengaged." There seems also to have been decomposition of a portion of the sulphate of baryta and sulphate of lead by means of silica, which, it is well known, has the power at high temperatures of displacing sulphuric acid even when combined with the strongest bases, with the formation of an equivalent proportion of silicates. The chief result of the agglomeration process is the combination of silica with the protoxides of lead and iron; and it is this point which constitutes the particular interest of the process. The reader is requested to refer to what has been previously stated in this volume concerning the reduction of silicates of lead by charcoal and metallic iron.

Blast-furnace.—There is nothing peculiar in its construction. It is rectangular in horizontal section, and at the lower part is $0^m 90$ (2′ 11·43″) wide and $0^m 60$ (1′ 11·62″) from front to back; the height from the mouth to the twyer is $1^m 60$ (5′ 1·32″); the hearth is of brasque, inclining forwards and downwards, and is $0^m 45$ (1′ 5·72″) below the twyer at the deepest part; there is a fore-hearth of brasque supported by cast-iron plates. There is only one twyer, $0^m 025$ (0·99″) in diameter at its eye, *i.e.* the end from which the blast escapes; the pressure of the blast is equal to a column of mercury $0^m 015$ (0·59″). The slag flows over the edges of the fore-hearth upon the ground, or is taken off in large solidified crusts. The lead

and regulus are tapped off into a lateral cavity in brasque. The gaseous products of the furnace in their course to the main stack pass through condensation-chambers, being propelled by a fan.

Method of proceeding.—A good mixture for smelting is composed as follows :—

	Kilogrammes.	
Roasted and agglomerated ore	1000	
Fluor-spar	100	
Limestone	240	
Scrap-iron	100	
Cupellation-furnace-bottoms, litharge, furnace residues	60	
Rich old slags	500	to 600
	1900	to 2000

Fluor-spar is never added in greater quantity than what is stated, as an excess of that flux, while it renders the slag very liquid, increases the loss by volatilization and the proportion of lead in the slag, in which, it is suggested, "the lead may probably be retained in the state of fluosulphate or fluosilicate," a suggestion wholly unsupported by chemical evidence. An excess of iron makes the slags very poor in lead, but causes frequent gobbing up. It has been remarked, that the larger the proportion of limestone in the charge, the poorer are the slags in lead. The consumption of coke is stated to be 15% of the agglomerated ore. When the ore has been properly roasted and agglomerated, no regulus appears on the surface of the reduced lead. The regular products of smelting are lead and slag, some regulus being occasionally formed.

The lead is said not to be very impure, but to contain arsenic, antimony, a little zinc and iron: it is very rich in silver, and in 1849 always yielded by assay more than 450 grammes per 100 kilogrammes, *i.e.* 147 ozs. per ton.

Regulus.—Two specimens of regulus have been analysed.

Composition of the Regulus.

	I.	II.
Lead	79·5	67·0
Iron	12·2	22·4
Zinc	1·1	1·1
Arsenic and antimony	4·2	4·5
Sulphur	2·3	4·0
	99·3	99·0

By dry assay specimens of these reguluses yielded :

	I.	II.
For 100 kil. of regulus—		
Lead	76 kil.	63 kil.
Silver	175 gram.	165 gram.
For 100 kil. of lead—		
Silver	230 gram.	262 gram.
Per ton of lead, about—		
Silver	75 ozs.	85½ ozs.

These two reguluses are designated as *mattes;* but as they differ notably in composition from each other, and as the proportion of electro-negative ingredients is very small for a true regulus or *matte*, it is probable that they were only mixtures of definite compounds intermingled, it may be, with metallic lead. In any case, it would be sheer waste of time to attempt to assign to them rational formulæ.

Slags.—They are generally dark-green or yellowish, compact, only slightly vesicular, and have a resinous fracture. It is said that their surface is often coloured brown from the peroxidation during cooling of the protoxide of iron which they contain. By dry assay they yield usually from 1% to 3% of lead, and when the smelting is difficult as much as 6% or 8%.

COMPOSITION OF THE SLAGS.

	I.	II.
Silica	38·0	40·0
Baryta	3·3	3·2
Lime	24·1	15·0
Magnesia, alkalies	2·9	3·2
Sulphuric acid	2·1	2·3
Fluorine	*	*
Alumina	1·4	1·7
Protoxide of iron	19·2	18·7
Oxide of zinc	1·6	1·5
Oxide of lead	6·0	13·1
	98·6	98·7

* Present in notable quantity, but not determined.

I.—Slag from the furnace when in good working order. II.—Slag from the furnace working irregularly. By dry assay these specimens of slag yielded:

	I.	II.
For 100 kil. of slag—		
Lead	1·50 kil.	9 kil.
Silver	0·75 gram.	3·60 gram.
For 100 kil. of lead—		
Silver	50 gram.	40 gram.
Per ton of lead, about—		
Silver	16 ozs.	13 ozs.

In No. I. the oxygen of the silica = 19·731, of the bases other than oxide of lead = 13·542, of the sulphuric acid = 1·258, and of the lead = 0·430. The oxygen of the oxide of lead is about $\frac{1}{3}$ of that of the sulphuric acid, *i.e.* in the proportion required to form PbO,SiO^3. Supposing the sulphuric acid and oxide of lead to be present in combination with each other, then the oxygen of the silica is to that of the other bases as 20·988 : 13·542, or nearly as 3 : 2; so that, inclusive of alumina, the composition is approximately represented by the formula $2RO,SiO^3$.

Smelting costs :—

	Francs.
Coke, 150 kil. at 7 f. 50 per 100 kil.	10·75
Preparation of charges for smelting	0·35
Smelters, by piece-work	2·00
Wear of tools, repair of furnaces, removal of slags, &c.	0·95
Per 1000 kil. (say about 1 ton English) of roasted and agglomerated ore	14·05
	s. d.
About	11 0

The raw ore may be estimated to contain approximately from 30% to 33% of lead.

In 1849 were produced at the Pontgibaud Works 1,258,708·45 kil. of lead, inclusive of litharge, *i.e.* about 1259 tons, and 7652·346 kil. of silver, *i.e.* 239,120·52 ozs. troy. The net profit from Sept. 30th, 1848, to Sept. 30th, 1849, is stated as 30,622·87 francs, *i.e.* about 1225*l.*

It may be added that when Rivot and Zeppenfeld published their account of the works at Pontgibaud, coal, containing 5·5% of ash, cost 30 francs the ton, and other coal, containing 15·5% of ash, cost 20 francs the ton; coke of St. Etienne, containing 5% of ash, cost 75 francs the ton, and coke of Brassac, containing from 12% to 14% of ash, cost 20 francs the ton; old cast-iron cost about 130 francs the ton; granulated cast-iron and scrap wrought-iron cost from 170 to 180 francs the ton; fluor-spar cost from 15 to 16 francs the ton; and limestone from 21 to 22 francs the ton.

Conclusions from the preceding Analytical Data.

In the process of lead-smelting at Pontgibaud the objects sought to be attained are as follow:—

I. The oxidation of the galena and associated iron-pyrites and zinc-blende by roasting with access of atmospheric air.

II. The combination of the oxides so formed with the associated silica by raising the temperature after roasting sufficiently to cause agglomeration.

III. The reduction of the silicate of lead in the agglomerated product in a blast-furnace by the joint action of carbonaceous matter and metallic iron.

IV. The separation of the iron and other foreign matter in the ore in the state of siliceous slag.

Silicate of lead is only partially reduced by contact with solid carbonaceous matter or carbonic oxide at a high temperature for the reason assigned at p. 31, unless a flux be present which may combine with silica, and render it fusible. Oxide of iron is such a flux, or fluor-spar, or a mixture of lime and alumina. Metallic iron reduces silicate of lead even in the absence of carbonaceous matter: thus, $3PbO,SiO^3+Fe^3 = 3FeO,SiO^3+Pb^3$. Moreover, sulphate of lead is reduced by iron. It has been stated that when the ore is properly

roasted and agglomerated *no regulus is formed*, from which it may be inferred that the metallic iron in the smelting charge becomes wholly oxidized, chiefly at the expense of the oxygen in the oxide of lead, and in a lesser degree at the expense of that in the oxide of zinc; and, therefore, that it is not employed as an agent of desulphurization as it is in the Iron-reduction Process to be hereafter described. From these considerations it will be evident, that in the blast-furnace there are all the necessary conditions for the reduction of the lead in the roasted and agglomerated ore, namely, temperature, solid carbonaceous matter or carbonic oxide, lime, fluor-spar, and iron. It is not to be imagined that in furnace operations the precise conditions easily attainable in crucible experiments can be perfectly imitated. It is impossible, for example, in furnaces, that the iron used should be so intimately mixed with the materials undergoing smelting, and kept so during the process, as in the miniature and easily controllable operations of the crucible. The process of Pontgibaud is interesting and instructive as illustrating the effect of free silica in the smelting of galena.

LEAD-SMELTING AT VIALAS.

The process followed at Vialas is, according to Rivot, similar in all essential points to that of Pontgibaud, and comprises the operations of roasting and agglomerating the ore in a reverberatory furnace, and smelting the agglomerated product in a blast-furnace. The proportion of silver in the furnace-lead varies much, ranging from about 16 to 224 ozs. per ton. The locality, particularly with respect to fuel, is disadvantageous; and the motive power, which is water, fails at least during three months every year. Moreover, Rivot remarks, that "the workmen are in general badly fed, and have not the energy, skill, and power of endurance, which characterize English and Belgian workmen. Labour is cheap; but when the actual work done is compared with the number of hours of employment, the conviction arises that the mines and works at Vialas are, in regard to labour, under still more unfavourable conditions than in regard to fuel."[5] Yet it is satisfactory to note that "as to consumption of material (*consommations*—fuel, etc.), and loss, the method of Vialas will bear with credit a comparison with the various processes of treatment in blast-furnaces adopted in Germany."[6]

LEAD-SMELTING AT LA PISE.[1]

This locality is in the South of France (department du Gard). The ores are obtained from Pallières,[2] near Anduze, and from Sardinia: the vein-stuff of the former is quartz and iron-pyrites. The process of smelting is the same in principle as that of Pontgibaud,

[5] Principes Généraux, p. 574.
[6] Op. cit., p. 611.
[1] This description is taken from Gruner's Mémoire sur l'état actuel de la Métallurgie du Plomb, Ann. d. Mines, 6 ser. 1868, 13. p. 325.
[2] Rivot spells it Paillières.

and consists of the same series of operations, namely, roasting or calcination, agglomeration, and reduction in a blast-furnace. Roasting is conducted with much care in flat-bottomed reverberatory furnaces from 8 to 12 metres (26′ 2·96″ to 39′ 4·44″) long, and 2 metres (6′ 6·74″) wide; but not so as to cause complete fusion. An ordinary Castilian furnace, 1 metre (3′ 3·37″) in internal diameter, and 2 metres (6′ 6·74″) high, with 2 or 3 twyers, was formerly employed for reduction; but owing to the rapid corrosion of the interior, and the large loss from volatilization, a furnace of the following construction has been introduced, it is said, with advantage, after a trial of 2 or 3 years.

The furnace rests upon a socle or plinth, within a cylinder of cast-iron, in the middle of which is a brasqued circular hearth with a tap-hole leading from the bottom: the plinth is 1^m 90 (6′ 2·80″) in diameter, and 0^m 90 (2′ 11·43″) in height. Upon this plinth is a course of fire-bricks laid flat; and upon this course are fixed vertically four segmental plates of cast-iron, which together form the cylindrical outer casing of the furnace, at the level of the zone of fusion. These plates are 0^m 80 (2′ 7·50″) high, and from 1^m 15 to 1^m 20 (3′ 9·29″ to 3′ 11·24″) in internal diameter. In order to be able to alter at will the position of the twyers, the four plates are not set in contact with each other respectively, but are separated by an equal number of fire-brick pillars 0^m 25 (9·84″) wide, and 0^m 22 (8·66″) thick. In three of these pillars the twyers are placed 0^m 25 (9·84″) above the plinth, and at the base of the fourth a hole is left for the slag to flow off. The plates are flanged outwards at the top and sides, in order to hold the fire-bricks placed between them, and support those which form the upper part of the furnace; and at the bottom gutters or channels are cast-on instead of flanges: the flanges are 0^m 22 wide (8·66″). On the outside these plates have three horizontal channels cast-on, which are kept constantly supplied with water, so that it may overflow and drop from one to another, and finally into the channel at the base, whence it passes into a cistern. From 4000 to 5000 litres (880 to 1100 gallons in round numbers) of water are used in 24 hours for thus refrigerating. The upper part of the furnace, to the height of 1^m 80 (6′ 0·87″) above the top flanges of the plates, is built of fire-bricks laid flat-wise; and above the brickwork, to the height of 0^m 60 (1′ 11·62″), the shaft consists of wrought-iron, and is merely a prolongation of the sheet-iron jacketing of the brickwork underneath. The total height of the furnace above the plinth is 3^m 25 (10′ 7·95″). At this level the mouth is closed by a horizontal plate of cast-iron, in the middle of which is fixed a sheet-iron hopper 1 metre high, and of the same diameter as the body of the furnace, open at the bottom, but closed at the top by a flanged cover fitting in grooves (*trappe à charnière*); and at the side of the trap is a little chimney, 0^m 25 (9·84″) in diameter, for carrying off the fume which may not be drawn through condensation-chambers by the exhausting power of a high stack. The chambers communicate with the furnace by an inclined pipe, which proceeds from the annular space comprised between the sheet-iron jacketing and the hopper.

Generally only two twyers are used, of 0^m 05 (1·97″) in diameter, and with a pillar of blast of 0^m 03 (1·18″) of mercury. Before the furnace is lighted, the plates are coated internally with a layer of plaster of Paris (*plâtre*) 0^m 02 (0·79″) in thickness; but as soon as it is in operation, that coating is detached in pieces, and in its place is deposited a thin layer of scoriaceous matter and regenerated galena, which the external water congeals on the cast-iron. Smelting proceeds uninterruptedly for two or three months, and all that is required to be done during this period is to replace some of the bricks surrounding the twyers; and, indeed, the campaign might be further prolonged if the upper part of the furnace did not become constricted by deposited matter.

In charging, the fuel is put in the centre and towards the front of the furnace, and the ore-mixture in the form of a crescent along the space above the twyers. The flow of the furnace gases is so regulated by means of a valve in the eduction-pipe, that the tension of those gases is only a little below that of the atmosphere. The fumes thereby pass off unmixed with air; their volume is reduced to the minimum; they do not ignite, because the external air is not drawn in; and but little plumbiferous vapour is lost, even when the mouth of the furnace is opened for charging. Before the adoption of this arrangement, the gases often took fire, and even, when the mouth was dark, the deposit in the chambers occasionally ignited like tinder. At that time, it is stated, the deposit was light and voluminous, containing from 35% to 40% of lead; whereas now it is grey, metallic, and heavy, and contains from 50% to 60% of lead. The present loss in smelting is said to be 4% of the total lead, of which only 2% at most is due to volatilization. The fume amounts to 6% or 7% of the weight of the ore. Formerly, with open-topped furnaces, the loss was 7% or 8% of the total lead, of which half was by volatilization.

The ores of Pallières after roasting are stated to be composed on the average of 50% of oxide, sulphate, and sulphide of lead; 30% of oxide, with a small proportion of sulphide, of iron; and 20% of quartz; and to contain 40% of lead, with 110 grammes of silver per 100 kilogrammes. These ores are smelted with the addition of from 20% to 25% of a mixture of limestone and lime, from 3% to 4% of rich iron ore, and from 2% to 3% of cast-iron. It is sought to produce tribasic slag, consisting of 30% of silica, 40% of protoxide of iron, 20% of lime, 5% to 6% of alumina with magnesia, and 2% to 3% of oxide of lead. The sulphur in the slags ought not to amount to 1%, and the content of silver to 1 gramme per 100 kilogrammes (6 dwts. 13 grains per ton). The slag runs into a cast-iron pot mounted on wheels. When the ore has been badly roasted, a little regulus is separated, and the slag then contains sulphides. From 8 to 10 metrical tons of roasted ore are smelted in 24 hours, with a consumption of 25% of coke. The lead is tapped off twice or thrice in 24 hours.

At the commencement, an attempt was made to smelt in the blast-furnace unroasted sulpho-carbonates (so-called, *i.e.* mixtures of galena and carbonate of lead), in conjunction with less carefully roasted

pyritic galenas, and with larger proportions of cast-iron and iron ore, occasionally as much as 7% of cast-iron and 20% of red or brown hæmatite having been added; but the result was the production of highly argentiferous slags intermixed with regulus. The composition of such a slag (produced in 1863) was determined by Rivot, and is as follows:—

Silica	37·33
Protoxide of iron	30·27
Alumina	4·50
Lime	17·30
Magnesia	2·17
Protoxide of lead	2·45
Sulphur *	5·48
	99·50

Silver, 5 grammes per 100 kilogrammes.

* Chiefly in combination with iron and calcium.

The sulphur in another slag, obtained in 1864, amounted even to 9·9%; whereas since 1865 it has fallen to 1% or even ½%, and the silver to 0·5, or at most 1 gramme per 100 kilogrammes (6 dwts. 13 grs. per ton) of slag, the proportion of lead at the same time not amounting to 3%. But since that period unroasted sulpho-carbonates have not been smelted, and roasting has been more completely performed. Hence, Gruner concludes, that the essential condition of good working, particularly with respect to silver, is the most perfect elimination possible of the sulphur during roasting. The evil caused by the presence of sulphur cannot, he adds, be remedied by increasing the proportion of cast-iron, and oxide of iron acts as a flux. "It is the condemnation of the *mixed* method (*i.e.* with iron as an accessory agent of reduction), and the confirmation of the vices of the iron-reduction process. Hence in the process at La Pise, the addition of the 2% or 3% of cast-iron to the charge, which is still made, ought to be entirely suppressed, and an equivalent proportion of rich iron ore substituted for it."

It is contended by Gruner, that occasionally cast-iron acts simply as fuel (*combustible*); and in support of this view, he adduces the facts that at La Pise the consumption of coke fell from 25% to 22%, and 20% as soon as the proportion of cast-iron added to the charge was raised from 2% or 3% to 7%; and that in Pontgibaud in smelting ores, containing 50% of lead, the addition of 10% of cast-iron to the charge was attended with a consumption of 9% of coke, and the addition of 12% of wrought-iron, with only 7%. Gruner remarks that in neither case was a trace of regulus separated, the iron being oxidized; and that it would be much more economical to substitute an equivalent proportion of rich iron ore for metallic iron. Hence, an increase in the proportion of iron added to the charge was attended with a decrease in the same proportion of the coke consumed.

Now the calorific power of carbon, in the state of pure wood-charcoal, is, in round numbers, 2500, when it is converted into car-

bonic oxide by combustion in oxygen gas; but, as coke contains a notable quantity of ash, its calorific power, when similarly converted into carbonic oxide, would be considerably less. The calorific power of pure iron, when burned in oxygen gas is, in round numbers, 4000. Assuming that in the blast-furnace at La Pise, the carbon of the fuel chiefly escapes as carbonic oxide, it would follow that supposing, according to Gruner, the iron added to the charge to act in the cases above-mentioned exclusively as fuel, an increase in the proportion of iron should have been followed by a greater saving in coke than its own weight. It must, however, be acknowledged, that in such a comparatively rude instrument as a blast-furnace, theoretical precision in the matter of calorific powers and reactions is not to be expected. But where is the proof that metallic iron is directly oxidized by the blast under the circumstances in question, for in the notion of Gruner such oxidation is necessarily involved? Is not the action reducing, even of such a furnace as that at La Pise? Is not the main object of the smelting effected therein the reduction of the products of the oxidation of galena, and of any native carbonate with which it may be associated? If this be so, it is not easy to understand how direct oxidation of iron by the blast should occur *pari passu* with the reduction of oxide of lead. The oxidation of metallic iron by contact with this oxide in the blast-furnace is more intelligible; and we know that in the case of silicates of lead, while iron will with the aid of heat effect complete reduction of the oxide of lead in those salts, carbon will not (see p. 33 of this volume), unless a substance such as an oxide of iron be present, wherewith the silica may combine and form a fusible product. On this principle, the addition of oxide of iron to a smelting-charge, in which lead exists for the most part, if not wholly, in the state of silicate, may be explained.

In the sequel the use of iron, as an agent for the reduction or desulphurization of galena on the large scale, will be considered at great length: when employed for that object, a regulus rich in sulphide of iron must be produced; and as such regulus always contains lead and silver in notable proportions, after-treatment is required for their extraction, which is tedious and costly, involving in some cases numerous so-called repetition processes. Every one will agree with Gruner, that any method of lead-smelting attended with the formation of regulus should be avoided whenever it is practicable. But there are ores, such, for example, as are notably cupriferous, which can hardly be satisfactorily smelted without the formation of regulus.

SMELTING OF THE LEAD ORES OF COMMERN.[1]

The so-called Bleiberg of Commern is situated at the extreme northern end of the Eifel where the high ground formed by the

[1] For the description of the mode of occurrence of the ores, I am indebted to H. Bauerman, and of the smelting to Hochstätter.

Devonian rocks breaks off against the great drift-plain of the lower Rhine, in an outlying patch of the variegated sandstones (*bunter Sandstein*) of the Trias which covers an area of several square miles.

The ore, bearing lead, is a white sandstone situated in the middle of the Bunter formation; it is about 120 feet in thickness and covered by an equal amount of red sandstones and coarse conglomerates. Only the upper portion is, however, sufficiently rich to be worth working; it is charged with small concretions varying from the size of a pin's head up to that of a pea, composed of grains of quartzose sand cemented by galena. These concretions are known as *Knotten* and the rock itself as *Knotten Sandstein*. The roof, a coarse conglomerate, is called by the miners *Wacken Deckel*, and is wrought up to, but never removed in, the underground workings, although it often contains a certain amount of galena which encrusts the lower sides of the pebbles in the same manner as chalcedony and hyalite are found in basaltic gravels. In the upper beds large spheroidal concretions of brown iron ores, partly soft and partly consolidated, are very abundant; they are known to the miners as *Eisentuten;* they contain small quantities of chromium and vanadium and in some instances as much as 4% of titanic acid.

The workings are partly in open-cast and partly subterranean; when the cover or overburden is not more than a hundred feet, it is stripped and the rock is removed by a series of terraces, as in slate-quarrying; when however, as happens in following the deposit to the dip, the cover is of greater thickness, levels are driven and the bed is won by a system of irregular pillar-workings somewhat like that followed in the thick-coal of South Staffordshire. The rock, although soft, stands well underground, the levels being kept open without timbering; when broken, however, it crumbles readily, so that the nodules can be separated from the bulk of the sand by the use of drum-sieves worked by manual power. The former alone are sent to the surface, the waste sand being used to fill up the old workings.

The system of dressing consists in the first instance of an elaborate sizing by means of drum-sieves; the coarser sizes are concentrated by jigging and round buddles, while the finest slimes are passed through a siphon-washer, or current-separator, when the muddy water falling into a cylinder meets a stream coming from below. The heavier stuff falls to the bottom, while the lighter waste is carried off by the upward current. In order to obtain the whole of the lead it is necessary that each grain of sand in the nodules should be separated from the matrix. For this purpose light stamp-heads are used; the slimes produced are concentrated according to fineness either on round buddles or shaking-tables both of the ordinary and self-clearing patterns.

In addition to galena, the sandstone in places contains a notable quantity of carbonate of lead, which from its lower specific gravity can only be imperfectly collected. In order to be able to save it entirely or nearly so, new dressing arrangements have been recently

introduced, in which the treatment of the sand commences at a point 60 feet above the ground level. Blue and green carbonates of copper are also found in places; they are very irregularly diffused, and when present diminish the value of the ore which is largely used for pottery glazes.

The removal of the waste sand from the dressing-floors is effected by receiving it into wrought-iron railway-trucks having moveable sides of a similar construction to the cinder-tubs used at blast-furnaces. When filled they are drawn by locomotives to the waste-tips, where they are emptied. It is only by a contrivance of this kind, that the enormous quantity of waste amounting to more than a thousand tons of sand daily, can be got rid of, as the country is comparatively flat, and does not give sufficient outfall to allow of its being carried away by a flow of water.

The different qualities of slimes produced in the dressing-processes are mixed so as to yield from 60% to 65% of lead, corresponding to an approximate composition of about 75% of galena, and 25% of quartz. The greater portion of the produce is now smelted on the spot, but was formerly sent to the Stolberg and Westphalian Company's works, at Stolberg near Aachen, for smelting.

The annual production of lead from the Commern mines is very considerable. In the year 1864 the amount of ground broken was 1,204,953 tons (of 1000 kilogr.), which furnished 22,397 tons of dressed ore, corresponding to a produce of somewhat less than 2% of ore, or from 1·2% to 1·5% of lead (containing from 0·007% to 0·014% silver, *i.e.* from 2 ozs. 5 dwts. 18 grs. to 4 ozs. 11 dwts. 11 grs. per ton), per ton of sand.

Lead ores occur in the same formation, in a similar manner but to a less extent, further south in the High Eifel near Gerolstein, and also in Nottinghamshire[2] and Leicestershire. In the copper-bearing sandstone of Alderly Edge in Cheshire, which is also of the same age, lead is found in the state of oxidized minerals, with some galena. These facts are of interest as indicating the prevalence of a very peculiar condition of things favourable to the mineralization of a purely sedimentary rock over a large area during the deposit of the New Red Sandstone.

LEAD-SMELTING AT MECHERNICH, BLEIBERG, RHENISH PRUSSIA.

I am indebted to Hochstätter for the following account, from personal observation, (September, 1869) of the process conducted at the works belonging to the company called the "Actienverein für Berg- und Hüttenwesen zu Mechernich" (Mechernich Mining and Smelting Company).

[2] While resident in Nottingham, my native place, about 40 years ago, I obtained numerous specimens of sandstone, with thin layers of galena attached, from a sand-pit at Trowell Moor, which is situate on the coal measures about 4 miles west of the town.

The annual produce of the mine is about as follows:—

	Percentage of lead.	Centners. (1 ctr. = 50 kilogrammes.)
Potter's ore	62 to 80	35,000
White-lead ore	50 ,, 52	12,000
Common ore	58	380,000

The process of smelting consists of the following operations:—

I. Calcination as *sweet* as practicable.
II. Fritting and melting, so as to form silicate of lead.
III. Reduction of the silicate of lead in blast-furnaces.

Calcining and melting.—Both operations take place in the same furnace. The bed is 32′ long and 12′ wide, and near the fire-bridge is fashioned into a hollow or basin, the bottom of which communicates with a tap-hole, the temperature in this part of the furnace being sufficient to melt the calcined ore; there are six working holes on each side. There are ten such furnaces at these works. A charge consists of 30 centners of dried ore, and each furnace when in working order holds 6 such charges at a time. A fresh charge is put into the coolest part of the furnace, *i.e.* towards the flue-end, and remains there 8 hours, when the calcined ore near the fire-bridge being now melted is tapped off, and the charges in the furnace are moved successively towards the fire-bridge, each in its turn taking the place of the contiguous charge previously introduced. The ore is thereby subjected to a gradually increasing temperature, and every part of it remains in the furnace during 48 hours. Notwithstanding this arrangement with a view to complete calcination, some galena escapes oxidation and is tapped off along with the melted silicate of lead or *slagged ore*, as it will henceforth be designated. This product is vitreous and brittle, and more or less brown.

Reduction in blast-furnaces.—The furnaces are 4′ wide and 4′ from front to back, and 16′ high, inside measure; the hearth is closed and brasqued in the usual manner; and there are four water-twyers, two close together in the back-wall and one in the middle of each side-wall. There are four such furnaces. The pillar of blast equals 9″ or 10″ of water. The charge is 100 parts by weight of slagged ore, 50 of tap-cinder (*i.e.* puddling-furnace slags, nearly approximating to the formula $3FeO,SiO^3$), and 48 of limestone, with the addition of 8% of pig-iron, when much undecomposed galena is present. The mode of charging is the same as in iron-smelting furnaces, *i.e.* layer upon layer. The products are as follow:—

Pig-lead, containing about 0·02% of silver (6 ozs. 10 dwts. 16 grs. per ton).

Lead-regulus, containing about 10% of lead: it flows out along with the slag and collects at the bottom of cast-iron receiving-pots, which are conical, and after cooling it is easily detached from the slag.

Slag, yielding by assay from $\frac{3}{4}$% to 1% of lead; it is thrown away.

From 180 to 200 centners of pig-lead are furnished by each blast-furnace in 24 hours. The pig-lead is desilverized with zinc. The

lead-regulus is crushed, calcined, and smelted in admixture with secondary products several times, and the regulus ultimately produced is thrown away when it does not contain more than 2% of lead. The lead thus derived is used in the manufacture of shot.

Desilverization of the lead.—From 500 to 600 centners are melted in an iron pot, and $\frac{3}{4}$% of zinc are put upon the surface of the molten metal, the temperature is raised so as to fuse the zinc, and the whole is well stirred as usual. The metal is then left slowly to cool and at rest during 8 hours, after which the zinciferous crust is removed with a perforated ladle. A second portion of zinc, to the amount of $\frac{1}{4}$%, is added to the lead, and the same treatment, as just described, followed; and after the lapse of 8 hours a third and last portion of zinc, to the amount of $\frac{1}{2}$%, is added, and precisely the same treatment again pursued. Thus, in desilverizing from 500 to 600 centners of lead, $1\frac{1}{2}$% of zinc, or from 544 to 650 lbs. of zinc, are needed. The products are as follow:—

Poor lead, containing a little zinc.

Zinciferous crusts, or rich skimmings.

The poor lead is passed through blast-furnaces, like those used for the reduction of the slagged ore, with the addition of from 4% to 5% of tap-cinder and from 3% to 4% of coke. There are two furnaces specially erected for that purpose. The lead after this treatment, which has for its object the volatilization of the zinc, is poled and cast into moulds, when it is ready for sale. This lead, according to an analysis by Fresenius, contains 99·99474% of lead. This is a goodly array of decimals, which will probably be considered as savouring of affectation of accuracy.

The zinciferous crusts are liquated in inclined iron retorts; and the lead, which drains off, is again treated with a little zinc in the usual way. The zinciferous crusts from this treatment, and the residue in the retorts, both of which retain lead in notable quantity, are melted in a common blast-furnace with the addition of from 14% to 15% of tap-cinder, and from 8% to 10% of coke. The zinc is more or less completely volatilized, and rich lead is tapped off, poled and cupelled by the English process. After poling, it contains from 2% to 3% of silver.

It is stated that the economical advantage of this so-called new method of desilverization has not yet been established. The trial of Cordurié's steam process at the Mechernich Works has previously been mentioned.

LEAD-SMELTING AT THE MÜHLENGASSE WORKS.

The ores are calcined in reverberatory furnaces of the following dimensions: bed 22′ long, 12′ wide, and 2′ high in the centre to the roof: there are eight working holes on each side. The ore is dried for 2 or 3 days on iron plates, then mixed with from 3% to 5%—rarely 10%—of lime, and the mixture is calcined and melted in reverberatory furnaces as at Mechernich. The charge is from 43 to 53 centners. Each furnace contains six of these charges at a time, and

a charge is put in every 6 hours. The melted ore is tapped into open rectangular moulds mounted on wheels, the sides of which moulds may be removed and the blocks of slagged ore detached.

Too high a temperature near the fire-bridge should be avoided, as the melted mass would then become too thin and be liable to flow out through crevices in the sides. In 24 hours from 160 to 200 centners of melted ore are obtained with a consumption of from 25 to 36 scheffels of coal (1 scheffel = 1½ bushel English). Two workmen attend each furnace, and a shift lasts 12 hours. The smoke of the furnaces in its course to the stack, which is 132′ high, passes through a chamber 360′ long, 12′ wide, and 22′ high. The loss of lead in calcining and melting is 7%, without taking into account what is recovered from the fume deposited in the condensation-chamber. The smelting of the slagged ore is carried on in small blast-furnaces 4′ square and 16′ high. The blast is supplied by two twyers in the back-wall. The waste gases pass into a large chamber 20′ above the bed of the furnace. The furnaces are charged every half hour, and a charge consists of 560 lbs. of slagged ore, 600 lbs. of lead-slags and 175 lbs. of cast-iron. The fuel is coke. The mode of charging is the same as in iron-smelting blast-furnaces. In a shift of 8 hours, 18 pigs of lead of 124 lbs. each are obtained. As the charges are only measured and not weighed, there are some discrepancies between different statements published concerning the works in question. According to one account,[1] 100 centners of slagged ore are smelted with the addition of 10% of lime, 25 centners of oolitic iron ore rich in lime, 95 centners of lead-slags, and 3 centners of pig-iron in small pieces, with a consumption of 500 cubic feet of blast of 26 lines pressure of mercury. In 24 hours from 190 to 200 centners of slagged ore are smelted, with the production of 100 pigs of lead of 1 cwt. each.

The products of smelting are as follow:—

Metallic lead, containing ⅓ loth (1 loth = about ½ oz. troy) of silver per centner:

Lead-regulus, of which the quantity will be proportionate to the imperfection of the process of calcination:

Slag, which flows into cast-iron pots on wheels.

In 1860 were produced at this establishment 625½ lbs. (Prussian) of silver, and 37,655 centners of lead.

LEAD-SMELTING AT MÜNSTERBUSCH, NEAR STOLBERG.

The ores both from Commern and Stolberg are treated at this establishment, and the average assay produce of lead is 55%, containing ¾ loth of silver per centner of lead. The ores from Stolberg contain, in addition to silica, earthy bases, chiefly lime, in great quantity. These ores are calcined in double-bedded reverberatory furnaces, so as to produce fritting; but those of Commern are calcined in the manner before described.

[1] Preuss. Zeitschrift, 7. p. 226.

The charge consists of 100 parts by weight of the mixed calcined ores of Commern and Stolberg, 80 of tap-cinder, and from 4 to 5 of limestone. Smelting is effected in small blast-furnaces with a consumption of from 24 to 25 parts by weight of coke. The yield of a furnace in 24 hours is from 60 to 70 pigs of lead weighing from 120 to 130 lbs. each. When the process is properly conducted not more than 1% of lead-regulus is produced. This regulus is calcined and smelted, when a second regulus is formed, which contains from 3% to 4% of copper. All slags containing more than ½% of lead by assay are smelted over again. In 1860 the smelting works at Münsterbusch produced 2863 lbs. (Prussian) of silver, and 139,100 centners of lead.

COMPOSITION OF THE SLAGGED ORE, BY EICH.[2]

Silica	18·18
Protoxide of lead	71·80
Iron, estimated as sesquioxide	2·56
Alumina	3·87
Lime	1·12
Magnesia	0·37
Sulphur	0·49
	98·39

From this analysis, the slagged ore may be regarded as substantially composed of silicate of lead.

COMPOSITION OF THE SLAG FROM SMELTING THE SLAGGED ORE, BY OSANN.[3]

Silica	33·51
Alumina	6·64
Protoxide of iron	54·93
Lime	3·41
Magnesia	0·28
Protoxide of lead	2·04
Oxide of zinc	0·11
Sulphur	1·53
	102·45

LEAD-SMELTING AT EMS IN NASSAU.

At Ems, where the ore contains less silica than that of Commern, it is calcined alone until fritting occurs, and the fritted ore is smelted with the addition of 25% of tap-cinder, from 75% to 100% of lead-slags, from 8% to 10% of lime, and the same quantity of scrap-iron. Spathic iron ore, containing from 5% to 15% of lead, which is found in the mines belonging to this establishment, is employed occasionally as a substitute for tap-cinder and metallic iron.

[2] Berg- u. hüttenm. Zeit. 1859, p. 68. [3] Ibid.

LEAD-SMELTING AT BURGFEY.

Some of the poorest of the ores of Commern are smelted without previous calcination in admixture with 3% of lime, and the mixture is formed into bricks, which harden by exposure to the air. The bricks are broken into pieces of the size of the fist and smelted in a small blast-furnace (Krummofen) with the addition of tap-cinder.

IRON-REDUCTION PROCESS.

This is the "Precipitation Process" (Niederschlagarbeit) of the Germans, in which iron is employed as an agent of reduction of galena. Both sulphuretted and oxidized compounds of lead are completely reduced when heated with iron. The process has been conducted in low blast-furnaces, about as large as a North of England slag-hearth (Krummofen), and in high furnaces about 16′ or 20′ high. As in these furnaces the material operated upon is in contact with incandescent fuel, and is exposed to a continuous upward current of carbonic oxide—iron ores, iron-scale (*i.e.* hammer-slag), or basic silicates of protoxide, which yield metallic iron under those conditions of deoxidation, have been used wholly or partially as substitutes for metallic iron in the charge. It has already been stated that metallic iron is employed as an accessory reducing agent in the English reverberatory "Flowing-Furnace."

LEAD-SMELTING AT TARNOWITZ.

This process has nowhere been more thoroughly tried than at the Government works at Tarnowitz, in Upper Silesia, named Friedrichshütte; and, though it has been abandoned there, I shall record the experience obtained at those works, availing myself mainly of the excellent description of them by my friend, Dr. Wedding, of the Mining Academy of Berlin.[1] This description contains the history of the works from an early period, and is highly instructive, as showing how many attempts at improvement have been made during a long course of years at a single establishment, how opinions have from time to time changed respecting the value of the modifications effected, and how necessary it is to exercise caution in forming a judgment on the characters of metallurgical processes, even from the experience of so-called practical men.

The ores occur in Dolomite, of the Muschelkalk formation, and are stated to be very pure. The composition of two varieties of ore, from the Paul-Richard and Friedrich mines respectively, is given as follows:—

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[1] Zeitschrift für das Berg-, Hütten- und Salinenwesen im Preuss. Staate, 14. p. 139 *et seq.* The account which follows of the processes at present conducted at Friedrichshütte is by the manager, Teichmann. See also Karsten's 'System der Metallurgie,' 1832, 5. p. 157.

COMPOSITION OF ORE FROM PAUL-RICHARD MINE.

Sulphuric acid	0·403		
Lime	0·282		
Magnesia, Alumina, Sesquioxde of iron, Oxide of zinc	traces.		
Silica	0·826	.....	6·421%.
Alumina	0·540		
Carbonate of lime	0·715		
Carbonate of magnesia	0·663		
Carbonate of protoxide of iron	0·239		
Carbonate of zinc	2·753		
Carbonate of lead	44·951	...	34·887% lead.
Sulphate of lead	9·279	...	6·348% do.
Sulphide of lead	39·3207	...	34·077% do.
Sulphide of silver	0·0283	...	0·0247% silver.
	100·0000		
Total lead	75·312%		
Do. by iron-crucible assay	74·610%		
Difference	0·702		
Total silver	0·0247% = about 8 ozs. per ton.		

A little zinc has been found by analysis in the button of lead obtained in assaying the ore from the above mine in the iron-crucible; nevertheless the result yielded by this method of assaying comes very near that obtained by analysis.

COMPOSITION OF ORE FROM FRIEDRICH MINE.

Silica	0·570		
Alumina	0·198		
Sesquioxide of iron	0·085		
Carbonate of lime	0·576	.....	3·202%.
Carbonate of magnesia	0·354		
Carbonate of protoxide of iron	1·121		
Carbonate of zinc	0·298		
Carbonate of lead	23·601	.....	18·300% lead.
Sulphate of lead	11·531	.....	7·879% do.
Sulphide of lead	61·412	.....	53·194% do.
Sulphide of silver	0·05472	.....	0·047631% silver.
	99·80072		
Total lead	79·373%		
Do. by iron-crucible assay	78·700%		
Difference	0·673		
Total silver	0·047631% = about 15 ozs. 10 dwts. per ton.		

In the year 1787 iron seems to have been first applied as a reducing agent at Friedrichshütte—that is, 14 years after the same appli-

'cation had been made at smelting works in the Upper Harz,[2]—and the smelting was effected in blast-furnaces 20′ high, 2′ 6″ wide and 3′ deep (*i.e.* from front to back). On the average 100 ctrs.[3] of ore were smelted with the addition of $8\frac{2}{3}$ ctrs. of granulated cast-iron and 20 ctrs. of iron finery-slags (*i.e.* chiefly consisting of basic silicate of protoxide of iron similar to the slags from the charcoal-fineries of English tin-plate works), with a consumption of 236 bushels[4] (English) of charcoal; and the products besides slag were 43·73 ctrs. of lead and 51·75 ctrs. of regulus containing per centner from 53 to 58 lbs. of lead and from $1\frac{1}{4}$ to $1\frac{3}{4}$ loth (1 loth = about $\frac{1}{2}$ oz. troy) of silver. The regulus was smelted in a similar manner with $7\frac{1}{2}$ ctrs. of iron per 100 ctrs., and yielded 35·88 ctrs. of lead and 50·76 ctrs. of regulus.[5]

The results of experiments concerning the relative values of charcoal and coke as fuel led to the exclusive adoption of the latter in 1791, and the substitution of low for high furnaces. Moreover, when coke was used, the regulus was so poor in lead as not to be considered worth re-smelting; whereas when charcoal was used, the regulus after 4 or 5 successive roastings and smeltings still yielded a regulus containing a notable proportion of lead. The superiority of coke to charcoal is ascribed to the higher temperature which it developes.

Experiments were made with a view to ascertain, whether it would be more profitable to smelt the ore in the roasted than in the raw state; and the result showed that the reverse was the case, the yield being less and the consumption of iron greater.

Oxide of iron in the form of iron ore was tried, and not found successful, owing, it is alleged, to the temperature having been too low and the time too short to reduce it to the metallic state in its descent through the furnace. The latter condition may account for the fact, but not the former, as the temperature, in a low blast-furnace with coke as the fuel, would certainly have been sufficient to reduce oxide of iron, if time enough had been allowed for the purpose. It is interesting to note the date of this application of oxide of iron in the smelting of lead ores, namely, towards the end of the last century; for so recently as 1854 a patent was granted in England to Mr. W. J. Cookson for "An improvement in the reduction of lead ores," which consists in heating them in a furnace or crucible in admixture with metallic iron, or oxide of iron, or iron-pyrites, and a small quantity of alkali, or neutral salt, and carbonaceous matter.[6]

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[2] Berg- und hüttenm. Zeit., 1867, p. 5, *et seq.*, where is given an interesting historical account of the Upper Harz silver smelting works from 1554 to 1867.

[3] I presume the former Prussian centner is here referred to. 1 ctr. = 103·111 lbs. avoirdupois; whereas now 1 ctr. = 110·232 lbs. avoirdupois. I have not considered it worth while to reduce these weights to English weights.

[4] 156 scheffels. 100 scheffels, Prussian = 18·901 imperial quarters English = 151·208 bushels.

[5] See Karsten's Archiv. 1st ser. 6. p. 177. Ueber das Zugutemachen des Bleiglanzes in Schachtöfen mit Eisenzuschlag, auf der Friedrichshütte bei Tarnowitz. This paper contains the history of the Tarnowitz work, and has supplied Dr. Wedding with some of his details.

[6] A.D. 1854, March 8, No. 553. Abridgments of the Specifications relating to Metals and Alloys, 1861, p. 257.

Raw coal was tried instead of coke, whereby there was a saving of fuel; but the yield was lessened and the time of smelting prolonged.

One twyer was substituted for the two previously used, and the pressure of the blast increased, with favourable results. Since the beginning of the present century the process of smelting continued about the same until 1862, when smelting in the reverberatory furnace, of essentially the same construction as the Flintshire furnace, was introduced.

The ore was delivered in two states, large or coarse ore, termed *the ore*, and fine ore termed *Schliech*, which were smelted separately, the former in low and the latter in high blast-furnaces. The term "ore" was applied only to such as consisted of pieces varying in volume from ¼ to 4 cubic inches,[7] the rest constituting Schliech, which I will designate as slimes, though the term may not be strictly appropriate.

Description of the Low Furnace (Krummofen).—It resembled, as before stated, the common slag-hearth of the North of England (see p. 411); and consisted of a rectangular chamber, with hearth and fore-hearth: there was only one twyer from 1″ to 1½″ in diameter in the back-wall, slightly inclined downwards and forwards. The width (*i.e.* the distance from one side-wall to the other in the interior) was 1′ 6″ and the depth (*i.e.* the distance from the fore to the back-wall in the interior) was 3′; the height from the twyer to the top was 3′ 2″ (Lange says 3′ 6″); and the twyer was 1′ 4″ above the level of the fore-hearth.[8] The hearth was prepared with brasque composed of equal parts of coke-dust and clay. The slag flowed away through an opening in the upper edge of the fore-hearth, the metal through a channel from the lowest part of the hearth into a cavity in front, and the regulus into another similar cavity (Stichherd). The furnace was prolonged upwards in the form of a shaft, which was divided by means of transverse arches into a series of chambers for the condensation of fume, openings being left so as to cause the gaseous products of the furnace to pass through these chambers in succession before escaping into the open air. On removing the lowermost arch and building up the fore-part underneath, a low furnace might be converted into a high one; and accordingly, the furnaces were prepared alternately as low and high furnaces according to requirements.

The nose or slag prolongation of the twyer was from 8″ to 10″ long, and was formed by charging with some lead-slag, before beginning to add the regular smelting-charge.[9]

Method of proceeding.—In ore-smelting the charge was composed of 100 ctrs. of ore, from 15 to 16 ctrs. of granulated pig-iron, 12 ctrs. of

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[7] See an interesting paper by Lange in Karsten's Archiv. 2d series. 1851. 24. p. 430. Ueber einige Veränderungen, welche auf der Friedrichshütte bei Tarnowitz bei den dortigen Blei-Schmelzprocessen vorgekommen sind.

[8] The Prussian and English measures are so nearly the same, that I have not considered it necessary to reduce the foregoing numbers to English.

[9] Karsten's Archiv. 1st ser. 6. p. 182.

iron finery-slags, and 36 ctrs. of ore-furnace lead-slags. In a 12-hour shift 70 ctrs. of ore were passed through, yielding on the average 45 ctrs. of lead, which contained from $1\frac{3}{4}$ to 2 loths of silver per ctr., and from 18 to 20 ctrs. of regulus: the consumption of coke amounted to from 22% to 25% of the weight of the ore. According to Karsten the ores were dressed so clean as to contain at most not more than 8% or 10% of vein-stuff, and occasionally only 5%. The same authority gives the charge and yield as follows: 100 ctrs. of ore, 14 to 15 ctrs. of iron, 12 ctrs. of iron-slags, and 36 ctrs. of lead-slags. To smelt 100 ctrs. of ore 16 hours were required, and a consumption of from 48 to 50 cubic feet of coke: the products were from 67 to 68·3 ctrs. of lead, from 24 to 25 ctrs. of regulus, and from 30 to 36 ctrs. of unclean slags, fume, etc. The regulus by the method of assaying then practised yielded only 2% of lead, although by exact analysis it was found to contain from 7% to 8% of *sulphide* of lead. The proportion of lead in the clean slags, which flowed over the fore-hearth, did not exceed $1\frac{1}{2}$%, and was often much less (as found by analysis). The loss of lead, which it was difficult exactly to ascertain, inclusive of that obtained from the various accessory products, amounted to 12% of the lead contained in the ore or 17% of that actually extracted from the ore. The proportion of silver in the lead varied from $\frac{3}{4}$ to $2\frac{1}{2}$ loths per ctr. The unclean slags and other rich residua were smelted by themselves. The regulus which was regarded as free from lead, and a portion of the clean slags, were smelted along with the slimes.

Slime-smelting followed the campaign of ore-smelting in high furnaces, which, as above stated, were merely low furnaces surmounted with a shaft 20′ high from the twyer to the mouth. The furnace was never filled up to the mouth, and generally not higher than 12′ above the twyer. Very fine slime cannot be directly introduced into a blast-furnace without several evil results: its state of division is such that much of it would be blown out even by a blast of low pressure and find its way into the condensation-chambers above; and it might, it is alleged, be so driven into and incrust the fuel as greatly to impede combustion; but these evils may be obviated by mixing the slime with milk of lime, whereby after the lapse of 48 hours it becomes agglutinated into lumps sufficiently hard and dry for use.

An average charge in slime-smelting was composed of 100 ctrs. of slimes,[10] 32 ctrs. of raw or unroasted regulus from ore-smelting, 24 ctrs. of iron finery-slags, and 120 ctrs. of lead-slags, with the addition, according to the materials at command, of 20 ctrs. of furnace residua, and 12 ctrs. of granulated cast-iron. From 20 to 22 ctrs. of slime were passed through the furnace in a shift, with a yield of from 8 to 9 ctrs. of lead, containing from $2\frac{3}{4}$ to 3 loths of silver per ctr.; some worthless regulus was also produced, which was thrown away; and the consumption of coke amounted to about $44\frac{2}{5}$% of the material smelted.

After the completion of the slime-smelting campaign, unclean slags,

[10] Karsten states that there were two varieties, one containing from 40% to 50% of lead, and the other tough slimes containing from 30% to 35%.

and all the residua of various kinds, such as pieces detached from the hearth, furnace accretions, etc., were smelted in high furnaces, in conjunction with slags from the reduction of litharge, about 33% of regulus from slime-smelting, and between 7% and 10% of iron finery-slags. From 75 to 80 ctrs. of residua were passed through in a shift, and a furnace continued uninterruptedly at work during 3 weeks. The yield, according to the nature of the residua, was from $1\frac{1}{3}$ to 3 ctrs. of lead per shift, containing from $1\frac{3}{4}$ to 2 loths of silver per ctr.; the slags were thrown away as worthless. The consumption of coke amounted on the average to $12\frac{1}{2}$% of the total residua above specified, not of the total material smelted.

With respect to the smelting of the residual products, Lange gives the following particulars. The regulus was roasted *sweet* in heaps or otherwise. The charge was composed as under :—

	Centners.
Unclean slags, taken off in crusts after tapping, etc.	35
Agglomerated stuff detached from the interior of the furnace, etc.	5
Fume agglutinated by lime	5
Lead-regulus roasted sweet	25
Old lead-slags of the 15th or 16th century	30
Granulated pig-iron	2
	100*

* The sum is 102, so that there is an error in one of the items, but in which I cannot state.—J. P.

Such a quantity was smelted in one-and-a-half 8-hour shift, with a consumption of about $35\frac{1}{2}$ cubic feet of coal, *i.e.* about 1 ton 6 cwts., the yield of lead being from 4 to $4\frac{1}{2}$ ctrs. If the regulus were not previously roasted, fresh regulus would be reproduced in nearly the same proportion as that in the charge; and when limestone was added with a view to prevent this evil, other injurious effects followed, namely, the formation of sulphide of calcium, and insufficient slagging of the iron, whereby a ferriferous bear (Eisensau) was often formed in considerable quantity, with consequent choking up of the furnace; and, moreover, but little lead was yielded. There is always a very notable quantity of sand in the charge, which requires a suitable flux, such as iron finery-slags.[1]

Thus ended the operations of a year, and as at last only worthless products remained, and nothing was left for further treatment, it is not surprising, as Dr. Wedding quaintly remarks, that strangers came from far and near to learn this model process!

In 1807 the high furnace was again resorted to for ore-smelting, but with unfavourable results, as the yield of lead was less, the regulus richer, and the slag not so clean as that from the low furnace. In the following year the experiment was tried of agglutinating the slime by fritting at a gentle heat previously to its being smelted; and the general results were less yield and richer accessory products and residua. Iron ore was again tried in 1811 as a substitute for the

[1] Op. cit. p. 438.

metal itself and found wholly to fail, the yield sinking considerably in consequence, though there was a saving in coke; the oxide of iron of the ore in great part directly entered into the slag. The discovery next made at these lead works is probably one of the most remarkable, and shews how slowly sometimes improvements are effected in metallurgical processes, and how important it is to determine accurately by chemical analysis the composition of all products. Until 1813 the slimes had been smelted along with regulus, but in that year the practice was given up, for the regulus so obtained was found to be far richer in lead than the regulus forming part of the smelting-charge! The only reason that could be assigned for such an obviously wrong practice would be the production of *much less* regulus than that put into the furnace; but such is not stated to have been the case. In 1816 a Carinthian or Bleiberg lead-smelting furnace was built at Friedrichshütte for the purpose of trial, as it seemed to be well adapted for such pure ores as those of Tarnowitz. This trial, however, led to no result; nor was it likely to prove other than fruitless under the circumstances; for, according to Dr. Wedding, the furnace was constructed only from drawings without proper supervision, and the process was carried on by local workmen unskilled in the management of the Bleiberg furnace, who, according to Rivot, "are much less energetic than English workmen, because they are very badly fed and are paid much less."[2] The reason alleged for the failure was the easy fusibility of the ores, which it was attempted to obviate by the admixture of sand (of all things in the world the worst that could be applied), and only once was lime tried as a substitute. Hence it would appear that even in Government lead-smelting works in Prussia there was a period (1816) when a knowledge of metallurgical chemistry would have been very useful; and it can hardly be doubted that the importation of a few skilled Carinthian lead-smelters into the Tarnowitz Lead Works would have been desirable, notwithstanding the following remarks of Dr. Wedding concerning the introduction of the reverberatory furnace for lead-smelting into the same works in 1861:—

"The experience everywhere and at all times arrived at has been here confirmed, that in the introduction of a new branch of trade the most favourable result is obtained, when it is developed by home workmen under the guidance of practical experienced managers, and the engagement of all foreigners is avoided;"[3] and adds in a note, "especially has this also been the case in introducing the Bessemer process into Königshütte." Whether Prussia owes anything or not to the labours of foreign workmen within her dominions, shall not

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[2] Principes Généraux, p. 393.

[3] Op. cit. p. 157. The original passage is as follows: Man fand auch hier die Erfahrung bestätigt, die überall und zu allen Zeiten gemacht worden ist (so namentlich auch bei dem Bessemern in Königshütte), dass die günstigsten Erfolge bei einem neuen Betriebszweige erzielt werden, wenn unter Anleitung practisch erfahrener Beamten die eigenen Arbeiter ausgebildet werden und Abstand von jedem Engagement fremder Leute genommen wird.

here be the subject of enquiry; but this may be affirmed without risk of contradiction, that England has been much indebted to the labours of specially skilled foreign workmen, and indeed some of our most important manufactures have been introduced by means of foreign workmen.

The proposal of Berthier to add galena to the bath of lead in the German cupellation-furnace was tried at Friedrichshütte, but was "wrecked on the imperfect desulphurization of the ore and the very bad quality of the litharge." The loss of lead after working up all the intermediate products amounted to 7·09% against 5% in the usual method; but the loss of silver remained the same. In 1829 further experiments were made in a furnace similar in construction to a German cupellation-furnace, except that the bottom was made of coke brasque. At first 12 ctrs. of lead were introduced into the furnace, and when it was melted, 16 charges of ore, of $\frac{1}{4}$ ctr. each, were gradually added, the slag drawn, and further ore supplied to the amount of 10 ctrs.; a great part of the lead was tapped off, and fresh ore added. From 100 ctrs. of ore were produced 64 ctrs. of lead and 17 ctrs. of slags, with a consumption of about 156 cubic feet (Prussian, nearly the same as English) of pit-coal, *i.e.* about $5\frac{3}{4}$ tons (estimating 1 ton of coal = 1 cubic yard), or in round numbers about 1 ton of coal for 1 ton of ore. After the complete working up of the intermediate products, the yield of lead amounted to $69\frac{1}{4}$ ctrs. The process was condemned and abandoned, chiefly on account of the disproportionately great expenditure of time and fuel, and the bad quality of the lead from its contamination, it is alleged, with sulphur (!).

Blowing cylinders were substituted at Friedrichshütte in 1826 for bellows, and in 1833 raw pit-coal was substituted for coke with success. The coal is stated to be non-caking and inferior, yielding, according to Rivot, 12% of ash. The term "coal," it is well to remember, is very indefinite so far as composition is concerned. The pressure of the blast was increased by one-half, and the furnace worked "hotter and quicker."[4] The composition of the charge was 100 ctrs. of ore, 14 ctrs. of broken cast-iron in fragments of about 1 cubic inch in volume, 12 ctrs. or somewhat more of iron finery-slags, and 30 of lead-slags from ore-smelting. The yield was $64\frac{1}{2}$ ctrs. of lead, with a consumption of about 57 cubic feet of pit-coal, *i.e.* a little more than 2 tons. The accompanying regulus and slag contained respectively 10%, and 1% of lead. After further trials 66% of lead was obtained (from 100 ctrs. of ore), with a consumption of about $53\frac{1}{3}$ cubic feet of raw pit-coal, *i.e.* very nearly 2 tons; the yield of lead being 2% higher than with the best coke made in piles or open fires, and the consumption of coal $22\frac{1}{4}$ cubic feet less, computed inclusive of the loss of weight in coking.

Many other experiments with several different objects were per-

[4] See Karsten's Archiv, 2d ser. 1835, 8. p. 3. Ueber die Benutzung der rohen Steinkohlen bei allen Bleihüttenprocessen in Schachtöfen. By Mentzel. Friedrichshütte, Tarnowitz.

formed at Friedrichshütte, of some of which only does Dr. Wedding give any details. In 1843 an attempt was made to substitute roasted lead-regulus for metallic iron, which, though unsuccessful, led to the conclusion that it would be advantageous to smelt that regulus in the roasted, and not as heretofore in the raw, state; and it was accordingly roasted for that purpose in large heaps. In 1845, we are informed, that for ore-smelting the low furnaces were profitably replaced by high ones; for, although the consumption of fuel and reducing agent was far greater in high furnaces, and the regulus contained 1% more lead, yet the yield was greater, namely, 67·73% of lead, *i.e.* 2% more than in low furnaces. Lange states that the regulus from the high furnace, on account of the larger proportion of east-iron added, was not only greater in quantity, but contained more lead (9%) than that from the low furnace (8%). The comparative trials, which are recorded in detail by Lange, seem to have been most carefully made; and the ore with which each furnace was supplied during the course of experiment was taken alternately from the *same* heap.[5] The cost per ctr. of lead in the high and low furnace respectively, was 6 thlr. 5 pf., and 6 thlr. 7 sgr. 7 pf., *i.e.* about 17*s.* 5*d.* and 18*s.* 1*d.*

The foregoing statement of costs appears to have been incorrectly calculated by Lange, from whose data my friend Professor Brush, of the United States, has deduced the following account:—

In the High Furnace.

	Rthlr.	Sgr.	Pf.*
2100 ctrs. of ore produced 1422 ctrs. of lead at a cost of	624	5	9

The cost of smelting 1 ctr. of ore = 8·91 n. groschen = 10·69 pence.
The cost of producing 1 ctr. of lead = 13·17 n. groschen = 15·80 pence.
The ton of lead taken at 20·31 per ctr. cost £1 2s. 8d.
The yield of lead per 100 parts of ore = 67·71%.

* 1 £ = 6 Rthlr. 20 Sgr.
1 Rthlr. = 3s.
1 n. gr. = 1·2 of a penny.

In the Low Furnace.

	Rthlr.	Sgr.	Pf.
2700 ctrs. of ore produced 1727¼ ctrs. of lead at a cost of	643	11	5

The cost of smelting 1 ctr. of ore = 7·15 n. groschen = 8·58 pence.
The cost of producing 1 ctr. lead = 11·17 n. groschen = 13·40 pence.
The ton of lead taken at 20·31 ctr. cost £1 2s. 8d.
The yield of lead per 100 parts of ore = 63·97.

Difference in cost between the High and Low Furnace per ton of lead in favour of the latter, 4s. 1d.

For a given weight of ore the High Furnace produces 3·74% more lead than the Low Furnace.

From the preceding data it may be inferred that more lead is volatilized in the low than in the high furnace; and, consequently, it might be supposed that there would be a proportionately greater loss of silver in the former than in the latter, but this was proved

[5] Op. cit. p 431.

not to be the case, as equal weights of lead from each furnace gave by cupellation beads of silver of equal weight.

It is worthy of notice, as Lange remarks, that in the low furnace less iron suffices to yield pure lead and regulus free from lead than in the high furnace, which he explains by the fact that flame escapes from the mouth of the low furnace, and a partial roasting of the ore is thereby effected, which does not occur in the high furnace, except just at first after the preliminary heating when the ore is first introduced.

Experiments were made with the view of substituting roasted lead-regulus for iron finery-slags, which also succeeded; and so the old lead-regulus of former days came to be worked up with advantage. In addition to the saving of finery-slags, there was 2% less consumption of iron per 100 ctrs. of ore.

In 1848 rich argentiferous galena from the calamine mines in the district of Friedrichsgrube (Frederick Mine) was first delivered at the Tarnowitz Lead Works.[6] Ore-smelting was carried on in high-blast furnaces of the same altitude as previously, but trapezoidal in horizontal section, 1′ 9″ broad at the fore-wall, 2′ broad at the back or twyer-wall, and 3′ 9″ deep, *i.e.* from front to back, all inside measure. In 1857, for 100 ctrs. of ore were required 9·7 ctrs. of broken cast-iron, 9·8 ctrs. of granulated cast-iron, and 16 ctrs. of iron finery-slags, for which 91 cubic feet of pit-coal, *i.e.* about 3 tons 6 cwts., were consumed. The slags contained from 40% to 45% of iron, 20% of silica, and 10% of alumina, besides variable proportions of lime and magnesia. From 36 to 40 ctrs. of ore were smelted in an 8-hour shift. Slimes were smelted in the same kind of furnace, having been previously agglutinated by means of milk of lime; 100 ctrs. of ore required from 14 to 21 cubic feet of caustic lime; the other components of the charge were iron, iron finery-slags, lead-slags, and certain other products containing lead. Furnace residua (Abgänge) of various kinds, such as unclean lead-slags, lead-regulus, fume, etc., were smelted in the high furnace with addition of iron and limestone.

In 1862 the Flintshire reverberatory furnace came into operation, by which the expense of metallic iron was saved, the necessity of the great number of what Dr. Wedding properly designates "repetition-processes" was avoided, and the diffusion of the silver prevented. But the blast-furnace was retained for the smelting of poor ores containing under 70% of lead, and furnace residua containing lead; and the experiment was made of substituting coke for raw coal, when it was found that a saving of fuel was thereby effected, though it was necessary to abstain from using it, as the "nose" (*i.e.* slag prolongation of the twyer) could not be maintained sufficiently short, and be kept from extending too far into the furnace. The evil, however, was corrected by the adoption of water-twyers. The blast-furnace, with

[6] This galena is richer in silver than that of the mines in the same district, in which galena is not associated with calamine.

two twyers and a vertical dividing-wall, such as is described in the account of lead-smelting at Freiberg, was next introduced with advantage for the smelting of furnace residua, and is still continued; and the last of the apparently interminable changes at the Tarnowitz Lead Works is, we are informed, allowing the clean slag to run into iron vessels in order to obtain it more free from regulus, and that any mechanically-mixed particles of lead may subside to the bottom, and so be collected. Since 1862 the residue, or grey-slag, from the reverberatory furnace (in which both ores and slimes are smelted, containing 70% or more of lead), has been passed through the blast-furnace above mentioned. Somewhat more than 35 ctrs.[7] of such slag are obtained from 100 ctrs. of ore, which yield in the after-treatment 47·2% of lead. A smelting-charge for the blast-furnace is given as follows: 100 ctrs. of slag, 21·1 ctrs. of iron, 44 ctrs. of iron finery-slags, and 10·4 ctrs. of limestone, for which 29 ctrs. of coal were required. A tabulated statement of results compiled by Dr. Wedding is added, as it may be useful to British lead-smelters for comparison.

100 ctrs. of ores, inclusive of slimes, in the reverberatory furnace	6·4 cubic feet of caustic lime. 52·5 ctrs. of coal.
35·8 ctrs. of grey-slag from the above	4·33 ctrs. of iron. 15·75 ctrs. of iron finery-slags. 3·42 ctrs. of limestone. 10·39 ctrs. of coal.

Dr. Wedding informs me that 141,393 ctrs. of ore were smelted at Friedrichshütte in 1868, and that 4500 ctrs. of fume were collected, which yielded 2250 ctrs. of lead, of the value of 13,500 thalers or 2025*l*.

Observations.—It will probably be thought that too much space has been devoted to the Tarnowitz Lead Works, as the process there so long practised of applying metallic iron as the main agent of reduction, might be sufficiently described in one or two pages at most. The history of those works, so circumstantially presented by Dr. Wedding, may however be studied with advantage, though the task be wearisome; for it teaches a much-needed lesson of humility and caution to metallurgists, and may serve to warn and guide for the future. It is well that these works were conducted on Government account, or, in other words, that capital was supplied by the taxpayers. Had it been otherwise, we should probably have been deprived of the advantage of such an interesting and instructive narrative as that of Dr. Wedding. Private smelters, possessing ordinary prudence, who have only their own capital at stake, and regard a satisfactory return for that capital as of paramount importance, are inclined to be more circumspect in the management of their affairs, and less disposed to experiment for the benefit of mankind in general than officials of Government works.

[7] In 1863 the average annual proportion was 31·75%; in 1864 it was 20·64%; and in 1865 it was 15·92%. The average percentage of lead in this slag in those three years was 47·5, 45·3, and 38·8 respectively: these numbers were derived from assays made in the iron-crucible.

Tarnowitz lead, according to Löwig, contains 99·21% of lead, 0·02% of iron, and 0·03% of zinc; and according to Ziurek 99·883% of lead, and 0·018% of iron.[8]

Karsten calls attention to the fact that less iron was used for the reduction of the galena than theory would indicate; and he suggests that the following agents may contribute towards its reduction—the associated dolomite, the oxygen of the blast (at least in the low furnaces), and lastly, the iron finery-slags. With respect to the two last-named agents, there is reason to believe that the suggestion is well founded. But there is another remark by Karsten, which seems to merit particular attention, namely, that granulated pig-iron is less efficient as a reducing agent than pig-iron which has been slowly cooled and afterwards broken up, *i.e. cæteris paribus*, more of the former will be needed to reduce a given weight of sulphide of lead than of the latter, or, what is equivalent, the same weight of pig-iron, containing the same proportion of carbon, will reduce more or less sulphide of lead according as the carbon is present as graphite, forming *grey* pig-iron, or combined forming *white* pig-iron. It is desirable that this statement should be made the subject of further experimental investigation.

The use of iron finery-slag, according to Lange, is to supply oxide of iron as a base to the silica of the vein-stuff in the ore; but there can be little doubt that as this slag is highly basic, a portion of its oxide of iron is reduced to the metallic state, and so may contribute towards the separation of lead, whether present in the state of sulphide or oxide.

LEAD-SMELTING IN THE UPPER HARZ.[9]

After the preceding description of this process, as it was formerly conducted at Tarnowitz, it will not be necessary to enter into so much detail as would otherwise be needed concerning the manner in which it was carried on in the Upper Harz, where it has recently been displaced by another process, in which basic silicate of protoxide of iron is used as a substitute for cast-iron. Indeed, the following account may be regarded as introductory to the description of the latter process.

The Harz Mountains have been described as an island of palæozoic rocks—partially Upper Silurian, but chiefly Devonian and lower Carboniferous—rising out of a sea of the North German secondary strata.[10] The culminating point is the well-known Brocken, 3500 feet above the sea. "This and the neighbouring heights constitute a central granitic mass, around which the palæozoic rocks are folded, the metamorphic strata having but little development."[11] There are two groups of veins

[8] Berg- und hüttenm. Zeit. 1866, p. 84.

[9] The metallurgical processes of the Upper Harz have been fully described by Kerl in his comprehensive treatise, entitled "Die Oberharzer Hüttenprocesse," 2nd ed. 1860; and to that treatise I am chiefly indebted for my information on the subject, and I desire fully to acknowledge my obligation to its author.

[10] See Murchison's Siluria, 4th ed. p. 391.

[11] See the Metallic Wealth of the United States, by J. D. Whitney, 1854, p. 369. Die Erzgänge und Eisensteins-Lager-

in the Upper Harz, that of Clausthal and that of Andreasberg. In the Clausthal group the mass of vein-stone is made up of a breccia of the country, held together by calc-spar, brown-spar, spathic carbonate of iron, quartz, and sulphate of baryta. The principal ore is argentiferous galena, with some copper-pyrites and blende. The Andreasberg group of veins is exclusively in argillaceous and siliceous slate, and yields argentiferous galena, as well as various silver ores, strictly so called, such as dark and light-red antimonial sulphides and fahlerz.

"The valleys," writes Rivot, "are numerous and of little depth: the streams are not of themselves powerful enough to produce the motive force required for the mines, dressing-floors, and smelting works. It has been necessary to form ponds and construct gigantic canals in order to collect the waters and conduct them where they are used. The *ensemble* of these works is one of the *chefs-d'œuvre* of human patience and genius."

The ore is essentially galena, and the whole of it is smelted in the state of coarse powder, termed *Schlieg*, and what may be delivered at the smelting works in lumps is there reduced to such powder. But as the treatment of the ore in this comparatively fine state of division is attended with evils which have been previously specified, repeated attempts have been made at the Altenau Works to smelt the ore in small lumps (*Knörperschmelzen*), the results of which were increased consumption of fuel and diminished yield, owing, it is alleged, to the larger proportion of earthy matter, especially silica, left in the lumps, than in the *Schlieg*.

At the Clausthal and Altenau Smelting Works the mixture of ores prepared for smelting contains on the average from 54 to 56 lbs. of lead and 10 quints (1 quint = 5 grammes) of silver per centner (50 kilogrammes) *i.e.* 0·10% of silver (32 ozs. 14 dwts. per ton); while at the Lautenthal Smelting Works it contains from 62 to 64 lbs. of lead and from 9 to 10 quints of silver per centner. It is hardly necessary to add that the various ores are, as far as practicable, so mixed that the matrix of one may serve as flux to that of another.

The ores from the Clausthal and Zellerfeld lodes, after having been dressed to a greater or less extent, contained the following percentage extremes of the various constituents in seven analyses made by Brüel and Bodemann, and tabulated by Kerl:[1]—

Sulphide of lead	77·34	.....	96·14
Sulphide of copper (Cu^2S?)	trace	.....	2·07
Sulphide of iron	trace	.....	2·41
Sulphide of silver	0·09	.....	0·13
Sulphide of zinc	0·00	.....	1·33
Sulphide of antimony	0·00	.....	4·36
Alumina	trace	.....	5·13
Carbonate of lime	trace	.....	4·24
Carbonate of magnesia	trace	.....	0·23
Silica	0·53	.....	12·38

stätten des nordwestlichen Hannoverschen Oberharzes. Dr. Zimmermann. Karsten's Archiv, 2. R. 1837, 10. p. 27 *et seq.* Kerl, Oberharzer Hüttenprocesse, 2nd ed. 1860, p. 48. Rivot, Ann. des Mines, 4th ser. 1851, 19. p. 465 *et seq.*

[1] Op. cit. p. 17.

The ores and *Schlieg* delivered at the smelting works contain, according to Kerl, from 4% to 28% of copper and about 0·4 quint per ctr., *i.e.* 0·004% of silver.

Schlieg-Smelting.

Cast-iron is used and less is added than, according to theory, would suffice for the complete reduction of the galena in the ore. At the Clausthal Works in the ordinary smelting of *Schlieg*, it is desired to add the cast-iron in such proportion, that the reduced lead and the lead-regulus may in weight be as 4 : 3, or, better still, as 5 : 4; and this results from the addition of about 4·5 ctrs. of cast-iron to 1 rost (= 36 ctrs.) of *Schlieg*, the actual average production of lead and regulus being 18·5 ctrs. and 15 ctrs. respectively. But of this quantity of lead 4·5 ctrs. are derived from furnace residua, such as impure litharge, etc.,[2] forming part of the smelting-charges, so that only 14 ctrs. are, it is computed, reduced by metallic iron, *i.e.* 3·1 ctrs. of lead for 1 ctr. of cast-iron.[3] Experience has, it is alleged, shown that the greater yield of lead, namely, three times the weight of the cast-iron, occurs when the latter is employed in the proportion stated. The addition of a larger quantity of cast-iron increases the quantity of regulus and only in a slight degree that of the lead; and the reason assigned is, that the excess of iron enters the regulus and there remains intermingled without further acting upon the sulphide of lead combined with sulphide of iron. On the other hand, the addition of a smaller quantity of cast-iron is followed by less yield of lead and by regulus richer in lead.

In what is termed "rich lead-smelting" at Andreasberg, *i.e.* the smelting of ores containing from 2½% to 10% of silver, it is computed there should be from 2 to 3 lbs. (1 lb. = ½ kilogramme) of lead for 1 quint of silver; and in "poor lead-smelting," with less silver present, there should be from 4 to 5 lbs. of lead for 1 quint of silver.

The mixture to be smelted is prepared for every rost (= 36 ctrs.) of *Schlieg:* the materials are added successively, layer upon layer (*schichtenweise*), so as to form a truncated pyramidal heap with a rectangular base; the order is as follows: lead-regulus slags (*i.e.* slags produced in the special process of smelting this regulus), *Schlieg*, iron, lead products (*i.e.* impure litharge, Abstrich, etc.), *Schlieg*-slags (*i.e.* from smelting *Schlieg* in the process under consideration), *Schlieg*, iron, lead products, *Schlieg*-slags. In filling the barrows for charging the furnace, care is taken to remove the heap in vertical portions, so that the charges may be as uniform in composition as possible.[4] Agglutination of the *Schlieg* by milk of lime is not adopted, from want of space, it is stated, for afterwards drying the lumps.

The time required for the extraction of the silver and lead from all the *Schlieg* delivered at the smelting works in the course of a year is about 1¼ year, and for the extraction of the copper from 2 to 2½ years.

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[2] Accessory products from the German cupellation-process,—Abstrich, hearth-bottom, first and last litharge formed. [3] Kerl, op. cit. p. 376. [4] Ib. p. 380.

Smelting is effected in a blast-furnace (*Schliegofen*) similar in all essential points to what has been already described. There is only one twyer in the back-wall. The mouth of the furnace is in communication with a series of condensation-chambers.

Much importance is attached to the formation and maintenance of a suitable "nose," or slag prolongation of the twyer in these furnaces.[5] After the usual preliminary gradual heating and blowing-in of the furnace, the first consideration seems to be the nose; and with a view to its formation, slags, which experience has shown to have the requisite fusibility, are thrown in at the *back*, *i.e.* close to the back-wall, in which the twyer is fixed underneath, and the fuel is thrown in in *front*, *i.e.* close to the fore-wall. There are thus, as it were, two vertical columns in the furnace, one of fuel in front and one of slag behind. When the molten slag in its descent drops in front of the twyer, it is met by the blast from the latter, whereby it is cooled and blown out into a pipe or "nose." If, in the course of smelting, the temperature near the twyer, from one cause or other, rises too high, the nose melts away; and if it falls too low, the nose becomes unduly prolonged and contracted at the end. With coke as fuel it is more difficult to produce and maintain a proper nose than with charcoal. In iron-smelting furnaces there is no nose, or at least should be none. The uses ascribed to the nose are, preventing the twyer from burning away and protecting it from the corrosive action of sulphureous matters, preserving likewise that part of the back-wall through which the twyer passes from melting down, and delivering the blast towards the centre of the furnace. When the furnace is in right working order, the nose has a pretty constant length, say from 10″ to 16″; and when it is inspected at the back, as it may easily be through the twyer, it affords valuable information concerning the internal condition of the furnace. With reduction of temperature, it increases in length, becomes contracted and less pervious at the end, and the "eye" appears "dark;" with rise in temperature, it becomes wider and shorter, the "eye" appears "bright," and it gradually melts away.[6]

In the regular working of the furnace, the charges continue to be introduced as above stated, the fuel in front and the smelting-mixture at the back; and this is necessary when the process is to be conducted with a nose. It is asserted that if such a furnace as is used for smelting *Schlieg* were charged after the manner of iron-smelting furnaces, *i.e.* fuel and smelting-mixture in alternate horizontal layers, the reactions between the constituents of that mixture would be more restricted (how, we are not informed), the temperature in the hearth would be too high, a nose being in that case impossible, and as a consequence there would be great volatilization.

According to Kerl the signs of the furnace being in good working order are, a nose from 1′ to 1′ 4″ or even 1′ 6″ long, somewhat in-

[5] See first volume of Metallurgy, by the Author, under the head of Copper-smelting in Blast-Furnaces. [6] See Kerl, op. cit. p. 385.

clined downwards, porous or "starry" in front, but around dark; the mouth of the furnace is without flame; the column of smelting materials descends gradually and not by jerks; the slag, having a proper consistency, runs out regularly and easily; the blast acts thoroughly; and there is fuel behind the tymp-stone (*Vorsetzstein*), which closes the breast or fore-part of the furnace.[7]

The cause of too long a nose may be too heavy a burthen, *i.e.* too large a proportion of smelting-mixture relatively to fuel, which evil may be corrected by increasing the proportion of fuel. Bad or very ashy fuel, as might be anticipated, will produce the same evil; for this is tantamount to diminution of fuel, properly so called. The effect of too long a nose is not only to derange the operation of smelting, but to burn away the fore-wall in consequence of the blast then escaping much closer to it than usual. The effect of too short a nose is to lower the temperature near the fore-wall, and so cause the solidification and adhesion of masses to it as well as the hearth, which it may only be possible to detach by breaking through the fore-wall.[8]

The products of smelting are furnace-lead, lead-regulus, and slag.

Furnace-lead (*Werkblei*).—Kerl records five analyses of this product from the Upper Harz smelting works, in which the extremes per cent. of the foreign metals determined were as follow:—copper, present in all, 0·05–0·76; iron, present in three, 0·12–2·96; antimony, present in all, 0·01–3·46; zinc, present in two, trace–0·16.

Lead-regulus.—The lead-regulus produced in the Upper Harz is mostly compact, occasionally crystallized, blue-grey but soon tarnishing and acquiring the colour of magnetic-pyrites; it commonly resembles fine-grained, seldomer coarse-grained, galena in fracture, but it is unlike galena in being porous or vesicular. On the under surface of the crusts of regulus, which are lifted off the subjacent liquid lead, crystals of it $\frac{1}{2}''$ long or more have been found at the Lautenthal Works; and that is just the position where they might be expected to occur, the particles of regulus there solidifying slowly in contact with the bath of lead and having freedom of motion sufficient to arrange themselves in obedience to crystallogenic force.[9] These crystals in the interior have a perfectly metallic lustre, but on the exterior a dark brown-red colour, due to oxide of iron resulting from atmospheric oxidation of the sulphide of iron in the regulus. They have been examined by Gustave Rose, who has proved them to be cubical, though in consequence of unequal development they might

[7] Op. cit. p. 386.

[8] On this subject I have received the following note from an English smelter: "I have always found in working these small furnaces, that when the nose became too short, the principal trouble was, that the back of the furnace was burnt through, however carefully the slags were piled behind and the fuel in front. A lump sets in front, and from that a blast is deflected, which cuts through the back-wall as a blow-pipe flame would cut through ice. When these furnaces are out of order, it is very difficult to get them to go well again."

[9] An English smelter suggests to me that these crystals may have been derived from the sulphide of lead dissolved in the lead at a high temperature; and this, he thinks, is the more probable origin. He has often seen nice crystals so produced when regulus was absent from the surface. They would rise to the top and attach themselves to any regulus there existing.

at first sight be mistaken for rhombohedrons; they cleave like galena.[10] The crystals are said to vary in specific gravity from 9·0 to 6·11, and to be magnetic.

Composition of Lead-Regulus from Clausthal, Upper Harz.[11]

	I.	II.	III.	IV.	V.	VI.
Sulphur	15·34	17·5	16·12	20·45	25·65	23·82
Lead	73·34	63·0	52·27	48·81	39·79	41·50
Iron	9·90	19·0	28·32	27·54	34·82	34·05
Copper	0·39	0·2	1·42	1·73	0·54	0·36
Zinc	0·20*	—	1·56	1·02	?	—
Antimony	0·40	—	0·31	0·45	—	0·66
Silver	0·12	—	—	—	—	0·12
	99·69	99·7	100·00	100·00	100·80	100·51

* With nickel and manganese.

The regulus was in every case crystallized, except No. VI. I. By Brüel. II. By Ohme. III. By Joy, in Rammelsberg's laboratory; its specific gravity was 6·11. IV. By Rammelsberg. V. By Hahn. VI. By Bodemann; it was compact.

Composition of Lead-Regulus from Lautenthal, Upper Harz.[1]

	I.	II.	III.	IV.	V.	VI.	VII.
Sulphur	17·27	18·92	16·40	19·33	18·71	18·13	23·97
Lead	65·78	59·33	60·69	53·31	63·79	61·71	35·68
Iron	13·15	19·79	20·55	21·77	13·72	17·91	31·55
Copper	1·15	1·10	0·49	0·23	1·53	0·77	3·79
Zinc	0·67	0·17	0·55	2·25	2·25	1·30	—
Antimony	0·18	0·13	0·36	0·38	?	—	1·49
Arsenic	—	—	—	—	—	—	1·07
Manganese	—	—	—	—	—	0·18	0·25
Silver	—	—	0·11	—	—	—	—
	98·20	99·44	99·15	97·27	100·00	100·00	97·80

I. II. By Bodemann; crystallized. III. By Brüel; the same regulus as II. IV. By Bodemann; compact and from the same piece as II. V. By C. Bromeis; crystallized. VI. VII. From Andreasberg by Avenarius and Bodemann respectively.

From the foregoing tables it is clear, that the regulus produced in smelting *Schlieg*, or galena more or less finely-divided, in the Upper Harz, with metallic iron as the reducing agent, varies widely in composition; and, consequently, it cannot be generally expressed by any one formula. This subject has been carefully considered by Rammelsberg, who properly calls attention to the fact that lead-regulus, espe-

[10] Kerl, op. cit. p. 396. Gurlt, Uebersicht der pyrogenneten künstlichen Mineralien, 1857, p. 22.

[11] Rammelsberg, Lehrbuch der chemisch. Metallurgie, 2nd ed. 1865, p. 232.

[1] Rammelsberg, op. cit. p. 232. Kerl, in recording these analyses, gives slightly different decimals for some of the numbers. Nos. VI. VII. from Kerl.

cially when crystallized, contains a notable quantity of finely-diffused metallic lead, which to a certain extent may be separated by pounding and washing; and there is at present no method by which it can with certainty be wholly removed. Metallic lead, indeed, may be seen on the fractured surfaces of the regulus. He suggests that during solidification metallic lead may separate through the entire mass, just as metallic copper separates under similar circumstances in "blue metal" which is a copper-regulus consisting essentially of sulphur, copper and iron; and the suggestion derives support from Rammelsberg's own analytical experiments on the lead-regulus in question. The regulus, which he analysed (No. IV. of the first table), yielded by pounding and washing $8\frac{1}{4}\%$ of residue, containing much lead in the metallic state. Now, assuming the theory of the separation of metallic copper in "blue metal" to apply equally to lead-regulus, *mutatis mutandis*, there is one obvious point of difference between the two cases, namely, the relative fusibility of copper and lead in regard to their respective reguluses, lead-regulus solidifying at a temperature far higher than metallic lead, which is not the case with "blue metal" and metallic copper. Hence, supposing metallic lead to pre-exist mechanically diffused in lead-regulus while molten, it is easy to conceive that as the former becomes rapidly solid and the latter very slowly, the metal might be retained in very sensible proportions in the regulus; for, although these substances differ much from each other in specific gravity, yet some time would be required to enable the lead to subside, particularly if it were in a finely-divided state as it would probably be under the circumstances.

The sulphur in the analyses recorded above does not suffice to combine with the metals according to the formulæ PbS, FeS, Cu^2S, SbS^3; and the inferences which may be drawn from this fact, in connection with that of the presence of a notable and undetermined quantity of metallic lead in the regulus, are—1st, That one or more of the metals exist as lower sulphides than those of the formulæ above: 2ndly, That sufficient lead may be present in the metallic state to be compatible with these formulæ: or 3rdly, That lower sulphides and metallic lead may co-exist.

If the 2nd inference be correct, Rammelsberg computes, that, assuming the metals to exist as sulphides of the formulæ referred to, the proportion of metallic lead required to be present would vary from 3·56% to 34·13%. But he thinks the last named quantity so large as to justify the 3rd inference; and that lead and iron, one or both, may be present as Pb^2S and Fe^2S. Reasons have previously been advanced for doubting the existence of such a sulphide as Pb^2S, at least in the solid state; but the existence of several sulphides of iron lower than FeS has been demonstrated. Admitting that Pb^2S does not exist *per se*, it does not follow that it should not exist in combination with sulphides of other metals.

According to Hausmann, when this regulus is crystalline and apparently rhombohedral, the cleavage resembles that of galena; and he considers the mass as an aggregation of small cubes with nume-

rous interstitial spaces. Although the composition may be approximately represented by the formula PbS + FeS, yet he regards it as probable that the regulus consists only of an intimate mixture of sulphide of lead and magnetic-pyrites ($5FeS + Fe^2S^3$). In support of this view, he adduces the facts that the lead-regulus of the silver works of the Upper Harz is always strongly magnetic, and that it not unfrequently contains crystals of magnetic-pyrites.[2]

After weighing the evidence on this subject, it appears to me that the analytical data are all so much vitiated by the presence of metallic lead in unknown proportions as not to justify the proposal of a rational formula for lead-regulus. The problem is one of much scientific interest, and well deserves attention.

Kerl remarks, that, if the iron entered the regulus in the state of protosulphide (FeS), 4·5 ctrs. of cast-iron would have reduced 16·7 ctrs. of lead; and hence he concludes that part of it must exist in the regulus in the state of disulphide (Fe^2S).[3] In order to establish this conclusion, it would be necessary to prove, that, in the smelting of *Schlieg*, absolutely the whole of the furnace-lead obtained is reduced by the cast-iron added; but no such proof has been advanced. When we reflect upon the conditions prevailing in the interior of such a blast-furnace as is used in smelting *Schlieg*, and upon the comparatively very imperfect mixture of the materials of the charge, it seems to me we shall have no difficulty in understanding why the full theoretical reducing-power of the iron should not be exercised. There is no doubt, notwithstanding Nolte's observations to the contrary, that 1 equivalent of iron will reduce 1 equivalent of galena; but the experimental demonstration of the fact, even under conditions most under control and in the highest degree favourable to accuracy, requires precautions which it is exceedingly difficult to secure. The contact of the iron and galena should be most intimate; or, if not, every particle of galena should come in contact with iron at a suitable temperature for reduction. But is it possible that this should occur even approximately in the blast-furnace with a mixture of materials so coarse and imperfect as that employed? Then there is the error arising from the volatilization of the galena in the course of its descent in the furnace; for it is certain that some, not to say much of it, under the circumstances must become heated to a degree at which volatilization readily takes place, especially when it is exposed to the rapidly ascending and highly heated gaseous current of the furnace. Again, with respect to the cast-iron added, it can hardly be doubted that part of it must melt, drop, and reach the hearth without coming in contact with any sulphide of lead. Although it may be possible by experience to ascertain what the proportion of cast-iron should be under given circumstances to be most effective as a reducing agent, yet it is assuredly not legitimate to draw any such inference from the practical results of smelting, as has been done with regard to the

[2] Beiträge zur metallurgischen Krystallkunde. Göttingen, 1850.
[3] Op. cit. p. 376.

theoretical necessity of the existence of subsulphide of iron in the regulus.

Lead-speise, so-called, is, it is said, occasionally produced in small quantity at Andreasberg in the smelting of arsenical and antimonial silver ores, and remains adherent to the regulus.[4] Bodemann has given the following analysis of such a so-called speise:—

COMPOSITION OF LEAD-SPEISE SO-CALLED.

Sulphur	5·05
Arsenic	0·13
Antimony	1·24
Iron	2·58
Copper	0·34
Nickel	—
Lead	90·52
Silver	0·14
	100·00

This substance was probably only a mixture of speise, regulus, and metallic lead.

In subsequent operations, as in the treatment of cupriferous lead-regulus, speise is obtained which would seem to be very variable in composition.

Furnace accretions (*Ofenbrüche*).—According to Kerl, the incrustation which forms on the internal surface of the shaft, or in the hearth of the Upper Harz *Schlieg*-smelting furnaces, consists essentially of sulphide of lead, with which are associated in variable proportions other metallic sulphides, particularly those of zinc, iron, antimony, arsenic, cadmium, and silver, as well as oxidized metallic compounds.[5] Metalliferous, more or less melted heterogeneous masses (*Geschur*, *Gekrätz*), composed of metal, oxides, sulphides, &c., are extracted from the furnace, either during smelting or after blowing-out. They are stamped, &c., in order to separate particles of metal, and the other portion is generally smelted along with furnace-fume.

Sulphide of lead.—It has occasionally been found in these furnaces, after they have been blown-out, in comparatively large, well-defined, step-shaped cubes aggregated in hollow hopper-like clusters, similar to those of common salt produced by gently heating and evaporating its aqueous solution; and Kerl states that it also occurs in compact, radiated, fine or coarse-grained speise-like masses in crevices and joints of the hearth-bottom, or in the upper part of the interior of the shaft 5′ or 6′ above the tymp-stone.[6] On fracture more or less porosity will generally be observed, which is not the case in unchanged natural

[4] Kerl, op. cit. p. 399.

[5] Ibid. pp. 400 and 409.

[6] See Hausmann's Beiträge zur metallurgischen Krystallkunde, 1850, p. 9, from which the following extracts have been made. Amongst the accessory products of furnaces, blast as well as reverberatory, no other metallic sulphide occurs so frequently and so distinctly crystalline as sulphide of lead. It is not only met with in lead-smelting furnaces, but in others in which the ores treated contain galena as an occasional constituent. The mode of its occurrence indicates that it is the product of sublimation.

galena. Beautiful artificial furnace-crystals in my collection, like those above described, have a blue-grey tarnish, which Hausmann attributes to an exceedingly thin film of sulphate of lead. According to Kerl, such crystals have generally a steel-blue colour; but they also occur bronze-coloured, and less frequently green or yellow. The same author says that not seldom they are converted without change of form into sulphate of lead, gradually when left exposed to the atmosphere, and quickly by the combined action of air and heat; and further that sulphate of lead is frequently disseminated in *Ofenbruch*. Crystallized *Ofenbruch* from the Clausthal Smelting Works was found by Metzger to be composed as under:—

CRYSTALLIZED SULPHIDE OF LEAD FROM CLAUSTHAL.

Sulphide of lead	95·5
Sulphide of iron	3·2
Sulphide of antimony	2·5
Sulphide of zinc	trace
	101·2

From what has been advanced in a former part of this volume concerning the volatility of sulphide of lead, there can be little reason to doubt that the artificially-crystallized sulphide from the Upper Harz lead-smelting furnaces is, for the most part at least, the effect of simple sublimation. The sublimation likewise of sulphides of antimony and arsenic is equally intelligible. In the first volume of this work experiments are recorded, which indicate that blende is somewhat volatile at high temperatures. Plattner was of opinion that sulphide of zinc in furnace-incrustations was not the result of direct sublimation, and he thus explains its occurrence. Sulphide of zinc in the lower part of the furnace, being strongly heated in contact with solid carbonaceous matter, is decomposed with the formation of bisulphide of carbon (CS^2) and vapour of zinc, which rises, provided the breast of the furnace is closed and it cannot escape therefrom; the bisulphide of carbon is oxidized by the blast and converted into carbonic and sulphurous acids, which by contact with incandescent carbon are resolved into carbonic oxide and vapour of sulphur; the zinc and sulphur, both in the state of vapour, combine and are deposited as a crystalline incrustation on the internal surface of the shaft. Plattner accounted for the apparent sublimation of sulphide of iron, which is a fixed substance, by the passing of the vapour of sulphur, formed in the manner just described, over sulphide of iron in the act of melting, or only heated so as to be soft; and, in support of this view, he adduces the results of experiments on the small scale, in which the vapour of sulphur was passed over sulphide of iron heated in highly refractory glass tubes.[7] Now, it is well known that in all blast-furnaces a considerable quantity of very finely-divided matter,

[7] Berg- und hüttenm. Zeit. 1855, p. 128.

composed wholly or in part of fixed ingredients, is carried upwards mechanically in the ascending gaseous current; and very finely-divided sulphide of zinc or of iron, especially when resulting from decrepitation, would find its way to the mouth of the furnace and more readily, for reasons assigned in the second volume of this work, along the inner walls of the furnace than elsewhere. But if this be so, then it is easy to understand how those sulphides should adhere to and accumulate upon the heated walls. It has previously been experimentally demonstrated[8] that amorphous sulphide of zinc prepared by precipitation from solution agglutinates and becomes crystalline when strongly heated.

According to Kerl, the sulphide of zinc in the *Ofenbruch* of the Lautenthal lead-smelting furnaces is usually brown, yellow, and green, and occurs less frequently crystallized than in compact masses, which have a distinctly foliated fracture, are more or less porous, and present a bright adamantine metallic lustre on the cleavage planes. The foliated often passes into a radiated structure, with a thin line of demarcation between the two.

Arsenical compounds.—Arsenious acid, in octahedral crystals as well as compact, and realgar (AsS^2) have been found in cavities in the inner walls of the *Schlieg*-smelting furnaces at Andreasberg.

Alloy of antimony, copper and nickel.[9]—Hausmann found such an alloy in a porous antimonial leady mass, which had separated in a fore-hearth (*Stechherd*) of a *Schlieg*-smelting furnace at Clausthal. It was in acicular crystals, of a light copper-red colour with a strong violet tint; and a similar compound in tabular crystals has been met with in crystallized lead-regulus from the smelting works at Ems and Holzappel. According to Müller the alloy from Holzappel, which was found by Sandberger, had the following composition:—

Composition of Crystallized Alloy.

Antimony	58·57
Copper	32·73
Nickel	8·97
	100·27

This corresponds to the empirical formula $Cu^6Ni^3Sb^3$. Copper alloyed with antimony in certain proportions has a beautiful violet tint, and constitutes the Regulus of Venus of the old chemists; and well does it merit that appellation on account of the beauty of its colour. The properties of these alloys will be fully described hereafter under the head of Antimony.

Slags.—The slags produced in smelting *Schlieg* in the Upper Harz seldom occur crystallized or crystalline. They are not wholly decomposable by hydrochloric acid.[10] They consist of the usual ingredients, and vary notably in composition. In 19 analyses of these slags re-

[8] See 1st volume of this work, under the head of Sulphide of Zinc.
[9] Kerl, op. cit. p. 404. Poggend. Ann. 103, p. 526.
[10] Kerl, op. cit., p. 412.

corded by Kerl, the extreme percentages of the chief constituents are as under :—

Silica	59·86	.....	30·04
Alumina	10·36	.....	2·20
Lime	18·72	.....	3·26
Magnesia	1·81	.....	0·16
Protoxide of iron	37·72	.....	19·42
Protoxide of lead	14·13	.....	1·62

Protoxide of manganese, potash, soda, baryta, oxide of zinc, protoxide of copper (CuO), oxide of antimony, arsenious acid, sulphide of iron, sulphide of zinc, and sulphur, appear as occasional constituents of those slags, but only in small proportion. Slag produced when the furnace was working thoroughly well (*von sehr gutem Ofengange*) had, according to Bodemann, the following formula :—

$$\overbrace{3CaMgPbO}{,}SiO^2+4(3FeO,2SiO^2)+Al^2O^3,SiO^2.$$

Smelting of Regulus.[11]

This process consists of two operations, namely, roasting and fusion of the roasted product in a blast-furnace, with the addition of metallic iron as a reducing agent. After what has already been stated in this volume, the theory of those operations will be understood.

Roasting.—The regulus is broken into pieces of about the size of the fist, which are piled up on a layer of pine-wood in the form of truncated pyramidal heaps, each containing from 1500 to 3000 ctrs., *i.e.* from about 75 to 150 statute tons. The ground underneath should be solid and flat, and covered with pounded *Schlieg*-slag to the height of 2″ or 3″. The wood at the bottom is ignited, and afterwards combustion is kept up in the mass by atmospheric oxidation of the sulphides composing it. After the lapse of from 2 to 4 weeks combustion ceases of itself, owing to the diminution of sulphur, which has mainly served as fuel, and to cooling from without. The heap is then turned over, the mass broken up, and the raw separated from the well-roasted lumps. The whole is again roasted or fired, the raw lumps being placed on the layer of wood at the bottom intended for ignition: this second firing lasts from 1 to 2 weeks. The heap is turned over and fired 6 or 8 times consecutively, the period of each successive firing becoming shorter and wood fuel being supplied at each operation. Lumps of properly-roasted regulus are described as brownish or blueish-grey, earthy in appearance, and porous and drusy on the surface, presenting efflorescence of sulphates and knot-like excrescences.[1] After all these firings the product still contains sulphides. In the smelting of roasted regulus other regulus is produced, which, preparatory to further treatment, is also roasted in the manner just described, but in smaller heaps. This

[11] Kerl, op. cit., p. 416 *et seq.*

[1] Ibid. p. 416. Eine poröse drusige Oberfläche mit aufsitzenden Vitriolen und knospenartigen Auswüchsen.

method of roasting in lumps piled in large heaps, is more imperfect than roasting the powdered material in the reverberatory furnace, but it costs less than the latter both in fuel and wages; and the roasted product being in lumps is preferable for smelting in a blast-furnace to the same product in powder, notwithstanding it be not so "sweet," or in other words, less completely deprived of sulphur in the state of sulphide. It need hardly be remarked that even in the management of such a seemingly simple and rude operation as that of roasting in heaps, some experience is required: and that, as the character of the combustion will vary somewhat, according to the nature of the sulphides forming the regulus, so corresponding modifications may be necessitated in conducting the process. As a general rule it may be stated that the larger the proportion of sulphide of iron present, the more easily and quickly will combustion be effected. Care should in every case be taken to prevent the temperature rising so high as to agglutinate the lumps firmly together in masses.

Composition of roasted regulus.—Kerl, if I mistake not, does not give any analysis of this product of the Upper Harz lead-smelting works; and as he has exhaustively described and has had peculiar opportunities of studying the metallurgical processes there carried on, it is presumed that no such analysis exists. The regulus consists almost wholly of two sulphides, namely, those of lead and iron: and the chemical changes which they undergo in the process under varying conditions of temperature, with free access of atmospheric air, have been previously considered. Sulphide of lead is converted into a mixture of protoxide and sulphate of lead. Sulphide of iron is converted successively with increasing temperature into sulphate of protoxide, sulphate of sesquioxide, and lastly into sesquioxide. The changes which take place in roasting disulphide of copper and sulphide of zinc have been fully considered in the first volume of this work; the final products of both are oxides.

According to Plattner the outer part of a thoroughly roasted piece of lead-regulus is richer in lead than the central.[2] We are indebted to Plattner for the following observations of interest on the occurrence of sulphate of lead in this regulus. "When lead-regulus contains much sulphide of lead in admixture, already after the first firing sulphate of lead of a white colour is found in the interstices between the pieces of regulus, partly as a loose crystalline lustreless powder, partly in clustered dull portions, partly in delicate more or less shining transparent needles and plates, and partly also, especially in the upper third of the roast-heap, in aggregations of well-defined hollow step or hopper-shaped cubical crystals. In heaps of roasted rich lead-regulus the interstices are in many places, particularly where during roasting the heat was pretty strong, often completely filled with light flocculent and occasionally crystallized sulphate of lead." Plattner explains the formation of this sulphate by the sublimation of sulphide of lead during roasting from the individual pieces of regulus, and its oxidation

[2] Die metallurg. Röstprozesse, p. 1856, 201.

partly while still in the state of vapour and partly after its condensation, either by atmospheric oxygen or by vapour of sulphuric acid, especially what is produced from sulphurous acid by contact action.[3] The cubical crystals of sulphate of lead above mentioned are when broken in two sometimes found to consist wholly of sulphate and oxide of lead, while at other times they contain a kernel of unchanged sulphide of lead. They are in fact pseudomorphs of cubes of galena, and consist of about 80% of sulphate of lead and 20% of free oxide. Plattner remarks that the fact of only a small quantity comparatively of free oxide resulting from the oxidation of the crystals of sulphide of lead, indicates that oxidation is chiefly effected by means of sulphuric acid in vapour. On opening the heap the sulphate of lead formed from crystallized sulphide appears white throughout and retains its whiteness; while on the contrary, that which has resulted from the oxidation of the vapour of sulphide of lead, appears also at first white, but on exposure to moist air frequently acquires a greenish colour, due to the presence of a small quantity of sulphatized oxides of copper and iron.[4]

The sulphate of lead formed out of the sublimed sulphide contained silver, which in the larger crystals Plattner found to amount to 0·004%;[5] and in the partially-crystallized sulphate from a deeper part of the heap he found as much as from 0·02% to 0·025%,[6] the proportion being very variable according to the content of silver in the lead-regulus before roasting. Hence he concludes that some sulphide of silver had been sublimed along with the vapour of sulphide of lead, though it is fixed when heated alone; and, consequently, that argentiferous rich lead-regulus should not be directly roasted, but previously freed from the greater part of its lead and silver by smelting with the addition of suitable matters.

A thoroughly roasted piece of lead-regulus will always, according to Plattner, be found to contain less silver in the middle than at the surface; and pretty nearly in proportion to the lead in those parts respectively. The greatest difference which he met with was in a lump from the Freiberg Smelting Works, of about 10 cubic inches in bulk, perfectly roasted throughout, the whole of the iron having been changed into proto-sesquioxide; it was very porous and loose in the middle, but from the surface inwards to the depth of about $\frac{3}{4}$", it was pretty dense and firm owing to the presence of free oxide and sulphate of lead which had been melted; this piece contained in the middle 0·075% of silver and 5·2% of lead, and at the surface 0·230% of silver and 17·2% of lead.[7]

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[3] See first volume of this work on the roasting of disulphide of copper.

[4] Hausmann states that he has never seen pure sulphate of lead produced in lead-smelting in reverberatory furnaces; but that he has not seldom met with it in the roast-heaps of lead-regulus in the Upper Harz Silver Works, partly crystallized and partly in a clustered and drop-like form. Beiträge zur metallurgischen Krystallkunde. Abhandlungen der königlichen Gesellschaft der Wissenschaften zu Göttingen, vol. 4, 1850.

[5] 0·4 pfundtheile in the centner of 100 lbs. = 50 kilog. = 10,000 pfundtheile.

[6] *From 2·0 to 2·5 pfundtheile per ctr.*

[7] Röstprozesse, p. 205.

The foregoing data suggested to Plattner the following practical indications: The roast-heap should not be too low or too flat, as it is desirable the vapours rising from below should be condensed in the upper part; on the other hand, it should not be too high, for in that case the circulation of air would be too active; and, lastly, it would be advantageous to cover the free pyramidal sides of the roast-heap in order to check the escape of vapours therefrom.

Smelting of roasted lead-regulus (*Durchstechen des gerösteten Bleisteines*).[8] —It is effected in low blast-furnaces (*Halbhohöfen* or *Krummöfen*), with coke, or coke and coal. The composition of the smelting-mixture or charge varies considerably at the different works in the Upper Harz. As the roasted lead-regulus contains a large quantity of oxide of iron, which must be slagged off, *Schlieg*-slags not saturated with base are added with that object, tribasic silicates being produced. Granulated cast-iron or old iron is employed to aid in reduction at only some of the works. By increasing the proportion of iron, the resulting regulus is indeed poorer in lead; but a large quantity of sulphide of iron is then formed, which increases the residual content of silver in that regulus. This silver, however, has to be extracted from the fresh regulus by smelting the latter in conjunction with matters capable of yielding lead; on which account it is preferable to use less iron for reducing and to obtain a regulus richer in lead suitable for desilverization. At the Lautenthal Works the roasting of lead-regulus having been conducted with more exactness and care, it has been found practicable to dispense wholly with the use of metallic iron, without at all lessening the yield of silver. At the Altenau Works limestone is used instead of iron, and serves probably to facilitate the reduction of metallic iron from the slags added by its action as a powerful base to the silica of those slags.

The various residual substances containing lead, which are always produced in lead-smelting, and which have been so often enumerated, are treated along with roasted lead-regulus. It is better to add *Abstrich* containing antimony to the charge in *Schlieg*-smelting, as the portion of that metal which finds its way into the *Schlieg*-regulus, is volatilized in a greater or less degree from the latter by roasting, and any copper, which may be eventually extracted from the regulus, will be thereby improved in quality.

In the first smelting of roasted lead-regulus, a fresh regulus is produced which may be designated No. 2; and this is subjected to the same operations of roasting and smelting as the first, when another fresh regulus, No. 3, is formed; and so the process is repeated usually 4 times.[9] What copper may exist in the original regulus, No. 2, becomes concentrated in the last regulus obtained; and may be separated therefrom by processes described under the head of Copper-smelting.[10] The degree of roasting will influence the number of subsequent fusions, of which generally four suffice to extract the lead and

[8] Kerl, op. cit. p. 424 *et seq.* [9] Each operation of fusion is called "Durchstechen."
[10] See first volume of this work.

silver, and produce a final regulus containing copper suitably concentrated. The result might be hastened by roasting more strongly and adding more metallic iron; but great loss of copper, it is maintained, would then occur from the metal passing into the slag, and lead rich in copper would be obtained, accompanied with copper-regulus richer in silver, because the extraction of the silver does not take place proportionately to that of the lead on account of the presence of sulphide of iron, with which sulphide of silver has a strong tendency to combine.[1] At the Clausthal Works metallic iron is used in all four fusions of regulus, at the Altenau Works only in the third, at the Lautenthal Works in three, and at the Andreasberg Works in none.

A campaign of regulus-smelting is shorter than that of *Schlieg*-smelting, and lasts from 3 to 6 weeks at most. Owing to the more basic character of the slags produced in the former, the siliceous material constituting the interior of the furnace is more quickly corroded than in the latter.

Lead from regulus-smelting.—It is richer in antimony and copper, and consequently harder and more brittle, than that from *Schlieg*-smelting; and that from Andreasberg is richer still in copper, antimony, and arsenic, on which account it solidifies readily with a dull surface, and must be laded quickly.

Regulus from lead-regulus smelting :—

Composition of Regulus from Smelting of Lead-Regulus.[2]

	I.	II.
Sulphur	17·12	15·55
Lead	43·07	32·06
Iron	8·03	13·15
Copper	30·46	34·01
Antimony	0·74	2·67
Silver	0·12	0·07
	99.54	97·51

I. By Brüel; from the third fusion, *i.e.* No. 3 regulus, Clausthal Smelting Works. II. By Bodemann; from the fourth fusion, *i.e.* No. 4 regulus, from the same works.

Rammelsberg remarks that the sulphur required in addition to that stated in the formula to produce the usual sulphides is 2·13 and 6·58 respectively.

Slags from lead-regulus smelting.—They are stated to be either tri-basic or mixtures of tri- and bi-basic silicates. In ten analyses of such slags tabulated by Kerl the extremes per cent. of the chief constituents are as under :—

Silica	29·90	37·79
Alumina	3·12	9·98
Lime	2·07	13·63
Protoxide of iron	33·60	46·44
Protoxide of lead	2·34	21·56

[1] Kerl, op. cit. p. 429.

[2] Rammelsberg, Lehrbuch, 2nd ed. p. 236.

The other constituents recorded as occasionally present in small quantity are magnesia, potash, oxide of copper, oxide of manganese, oxide of zinc, oxide of antimony, and sulphur.

Lead-smelting by the Iron-Reduction Process in Japan.

Pumpelly has given the following account from personal observation.[3] The mines are at Ichinowatari, at the entrance to a rocky ravine containing a mountain torrent. The ore is galena, associated with zinc-blende, and iron and copper-pyrites. The body of the vein-stone is chiefly magnesite, while the rocks enclosing the veins are calcareous argillites and a greenstone. The ore is stamped by machinery similar in principle to that of Cornwall and Germany, though far less efficient. The stamped ore is washed in wooden pans, generally by women, whereby a very pure *Schlich* is obtained. A cavity in the ground, lined with a mixture of charcoal and clay, constitutes the furnace or hearth: it is about 14″ wide and 10″ deep, with under-drains. The blast is supplied by double-acting box bellows (see a description in the preceding volume of this work on Iron and Steel), and passes through a clay twyer; and in front, *i.e.* opposite to the twyer, there is a clay shield for deflecting the blast. The smoke and fumes escape through a chimney. The hearth is filled with burning charcoal, on which about 80 lbs. of ore are thrown. When the ore is about half melted, from 25 to 30 lbs. of pig-iron in small pieces are added, and when partial reduction has been effected, the contents are well stirred. About two hours subsequently, the charcoal is withdrawn, and water thrown into the hearth with a view of solidifying and taking off the regulus of sulphide of iron. This is repeated six or seven times, until indeed the lead becomes perfectly clean on the surface, when it is cast into bars. The regulus is thrown away.

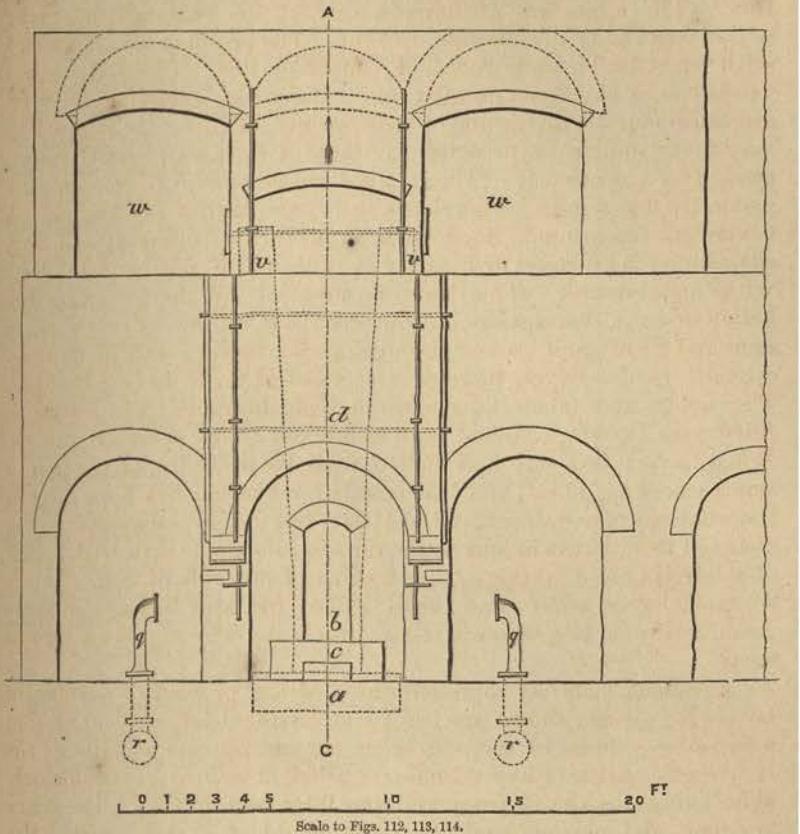
Excellent pictorial representations of the process of washing in bowls by women, and of smelting and casting lead, are contained in a Japanese volume in my possession, on mining and metallurgy: it is one of a series of five volumes, entitled 'Pictures of the Remarkable Things in the Country and the Waters of Japan.' The ingots are long and narrow, and the ingot-mould is a stone with a flat upper surface, in which are three furrows to receive the lead.

LEAD-SMELTING WITH BASIC SILICATE OF PROTOXIDE OF IRON.

The application of basic silicate of protoxide of iron in the form of iron finery-slags, as an agent in the reduction of galena, or sulphurized compounds of lead in the blast-furnace, has already been described, and its mode of action considered. Recently, however, a similar

[3] Across America and Asia. Notes of a five-years' journey around the world, and of residence in Arizona, Japan, and China. By Raphael Pumpelly, Professor in Harvard University (U. S.), and sometime Mining Engineer in the service of the Chinese and Japanese Governments 1870, p. 145.

silicate, produced in copper-smelting in the Lower Harz, and containing a sensible portion of silver, has been employed for this purpose with advantage in the Rachette furnace, a furnace to which only an allusion was made in the preceding volume of this treatise. A detailed account of the process has been published in Germany, of which I shall avail myself in the following description.



Scale to Figs. 112, 113, 114.

Fig. 112. Front elevation of Rachette furnace.

Description of the Rachette Furnace.—The furnace selected for description is that at the Altenau Smelting Works, near Clausthal, in the Upper Harz, with all the improvements made subsequently to its first introduction at those works in 1864:[1] it is represented in the annexed woodcuts, figs. 112, 113, 114, 115.

[1] My information on the subject has been derived from the interesting series of papers entitled "Neuerungen auf den Oberharzer Silberhütten" (Novelties at the Upper Harz Silver Works), in the "Berg- und hüttenmännische Zeitung," 1867. The annexed woodcuts are copied from the lithographs in the same volume after drawings by C. Ey.

This furnace differs essentially from other blast-furnaces in its horizontal section, being long and rectangular, and having a row of several twyers on each of its long sides, with a tap-hole at each end or narrow side.

a. Hearth-bottom, sloping downwards from the middle towards each end or narrow side of the furnace. *b*. Fore-wall. *c*. Fore-hearth. *d*. Hood for carrying off fume. Water-twyers are employed of which one is shown in fig. 118 in longitudinal section and end elevation: they are fed with clear water from a wooden cistern, A, fig. 116. The water enters A at the bottom through holes in the supply pipe, as shown at *f*, and flows out through the rose-top at *g*, through the pipe *h*; which arrangement has for its object the subsidence of mechanical impurities. From the pipe *h* water passes into the pipes *i i*, fig. 114, from which it rises through the pipes *k k*, &c., to the water-twyers *l l* &c., on each side; whence it flows hot through the short pipes *m m* &c., into the funnels *n n* &c., and thence into the water-blocks B B &c. These water-blocks are 1′ 8″ high, 4½″ broad, and 1′ from the interior of the furnace; the water flows out from them through the pipes *o o*. In order that the circulation of water may be regular, the water in the cistern is kept so high that there is a constant overflow from the waste pipe *t*. The cock *u* is simply for the purpose of emptying the cistern A. The blast passes from the main *p*, through the pipes *r r*, and thence to the vertical side-pipes *q q* &c., through leather connecting-joints to the blast-pipes into the twyers. The side-pipes are each provided with a throttle-valve regulated by the mechanism represented in fig. 117. The furnace is charged on each side of the mouth from the arched platforms *w w*, over the guard-walls *v v*.

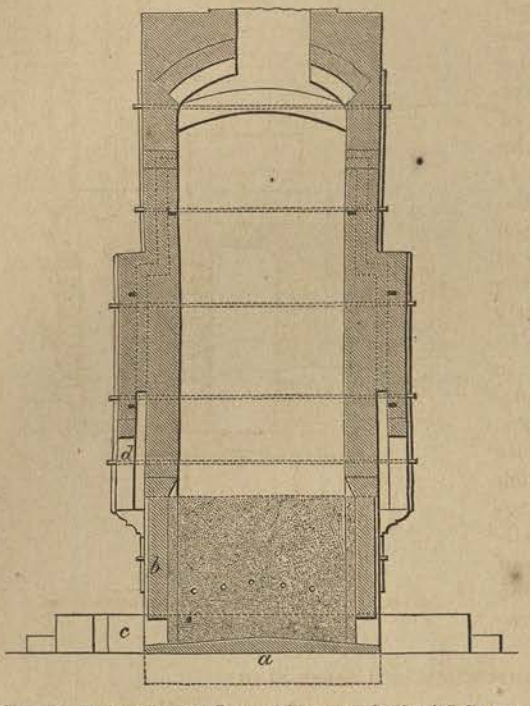


Fig. 113. Vertical section of Rachette furnace on the line A C, fig. 112.

The Rachette furnace erected in 1866 at the Lautenthal Smelting

Works is essentially the same as that described, differing only in a few minor details. In this furnace the solid brick or stone hearth-bottom, which is 2′ thick, is covered with three layers—the lowest pounded clay-slate, the next a mixture of pounded clay-slate and brasque, and the uppermost brasque alone. The sides of the hearth immediately above the solid bottom are of common brick to the height of 1′ 2″ 8 lines; then of sandstone to the height of 2′ 8″, in which lie the twyers; next of refractory lining to the height of 1′ 5″; and lastly of brick.

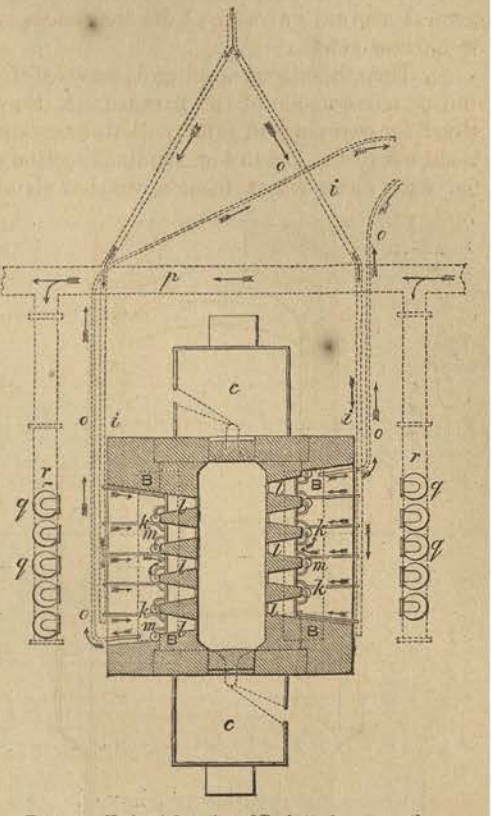


Fig. 114. Horizontal section of Rachette furnace on the line D E, fig. 115.

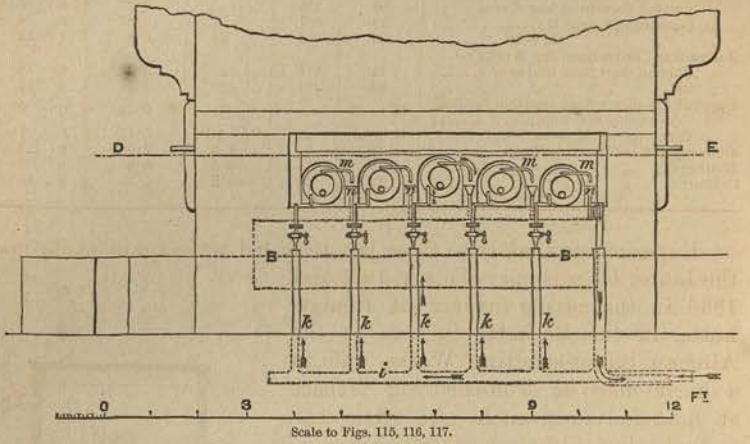
The copper-slag in question has been analysed by several chemists, whose results indicate that it does not vary much in composition, with respect to its chief constituents. Two analyses of it made by Streng in 1855 will suffice for illustration:—

Composition of Copper-Slag.

	I.	II.
Silica	17·17	16·95
Alumina	2·73	3·69
Protoxide of iron	69·84	70·27
Lime	3·27	3·37
Magnesia	0·83	1·30
Protoxide of copper	1·77	1·90
Protoxide of manganese	0·54	0·07
Oxide of cobalt and zinc	1·54	0·98
Sulphur	1·58	1·73
	99·27	100·26

In an analysis of a specimen of this slag by Breymann 1·99% of dioxide of copper (Cu^2O) is given; and there is reason to believe that when copper exists in the state of silicate in such a slag, it is not in a higher degree of oxidation than dioxide.

The slags analysed by Streng yielded by dry assay per centner (=100 lbs.=50 kilogrammes) 54 lbs. of cast-iron, 1·2 lb. of copper and 0·25 quint (1 quint=5 grammes) of silver, *i.e.* 0·025% or about 8 ozs. 3 dwts. per ton; and by assay in a charcoal brasqued crucible without addition of any substance 52% of cast-iron was obtained. These slags came from the Oker Smelting Works in the Lower Harz, and resulted from the smelting of thrice-roasted Rammelsberg copper ores with the addition of about $\frac{1}{10}$ of their bulk of roasted clay-slate, as much or somewhat more of roasted clay-slate infiltrated with copper ores, and slags in suitable proportion. Smelting was effected in a low blast-furnace.



Scale to Figs. 115, 116, 117.

Fig. 115. Twyer arch, or side elevation, of the lower part of Rachette furnace.

Interesting experiments have been made in order to ascertain the reducibility of the iron contained in the slags above mentioned of which analyses by Streng are inserted. A suitable composition for a smelting-charge having been found and sufficient pressure of blast given, slags were treated in a cupola-furnace at Altenau in March, 1865; and the products were slag quite free from copper and poor in iron, and white thickly-liquid cast-iron of the following composition according to Dr. Henkel:—

COMPOSITION OF CAST-IRON FROM COPPER-SLAG.

Graphite	0·11	0·95
Carbon, chemically combined	0·84	
Copper		2·42
Arsenic		0·03
Antimony		0·17
Silicon		0·98
Iron		92·53
Silver (1 oz. 6 dwts. 3 grains per ton)		0·004
Sulphur		1·47
		98·554

Assays have been made by Kerl of copper- and lead-slags, old as well as recent, from various smelting works in the Lower Harz and other localities, of which assays the following results are selected for the purpose of illustration :—

	Per centner (50 kilog.).				Silver per ton.		
	Cast-Iron.	Copper.	Lead.	Silver.			
	lbs.	lbs.	lbs.	quints.	ozs.	dwts.	grs.
Oker—Old copper-slags with green efflorescence from weathering action ..	54	0·96	..	0·1	0	6	13
„ Current copper-slags (*i.e.* as at present produced from a large average	54	1·25	..	0·1 to 0·2	0	6	13
					0	13	2
Sophienhütte (Sophia Smelting Works)—							
Current slags from mixed ores ..,	36	2·5	..	0·12	0	7	20
„ Lead-regulus slags	33	0·7	..	0·37	1	4	4
„ „ „ old heap.....	30	0·7	2	0·5	1	12	16
Juliushütte (Julius Smelting Works)—							
Current slags from lead ores	24	0·9	..	0·25	0	16	8
„ Old „ „	30	1·1	..	1·1	3	11	21
Upper Harz—Slags from smelting Schlieg (ore finely divided).....	25 to 30	..	3	0·15	0	9	19
„ Slags from regulus-smelting	44 to 46	..	1·5 to 2·5	0·11	0	7	5
Stolberg, Aix-la-Chapelle—Slags	30	..	2·5	0·06	0	3	22
Bleiberg „ „	40	..	3·5	0·06	0	3	22
Commern „ „	22	..	9·0	0·25	0	16	8

Experiments similar to those just recorded were again made upon the Lower Harz copper-slags in 1865 and 1866 in the cupola-furnace at Königshütte, in the Rachette furnace at the Altenau Silver-smelting Works, and in a high charcoal iron-smelting furnace at Rothehütte, in each case with coke as fuel; but, although nearly complete reduction of the iron in the slags was effected, yet the pig-iron produced generally contained too little carbon, and the consumption of fuel was too high. It was only at the Rothehütte, where the furnace was 32′ high, that strongly carburized foundry pig-iron was obtained, which was perfectly suitable for the finest ornamental castings. All these experiments led to the conclusion that it would be possible only in a coke iron-smelting furnace of suitable construction, and 40′ high, regularly to produce pig-iron having a high content of carbon and with sufficient economy in regard to fuel. Analyses of certain of the products found in the course of this investigation have been made by Streng, and as the results are interesting in a theoretical as well as practical point of view, they are here inserted.

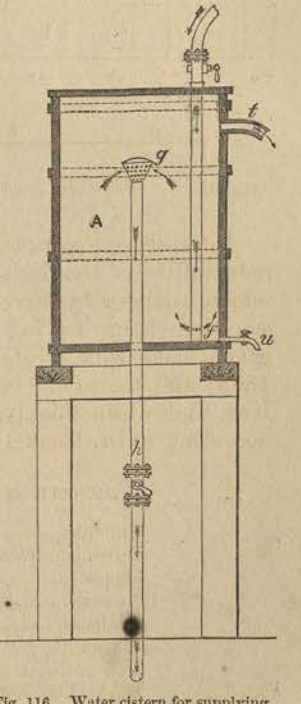


Fig. 116. Water cistern for supplying twyers of Rachette furnace.

CONSTITUENTS OF PIG-IRON FROM COPPER-SLAGS.

	Per cent. I.	II.
Carbon	1·40	2·46
Silicon	0·35	*
Sulphur	1.25	0·14
Phosphorus	0·22	*
Copper	2·36	2·20
Antimony	0·07	—

* Not ascertained.

I. From the Altenau Eisenhütte, Sept. 1865. II. From Rothehütte, April, 1866: it contained 0·25 quint of silver (= 1·25 gramme per centner of 50 kilogrammes, *i.e.* 1·25 × 20 = 25 grammes = about 16 dwts. per ton).

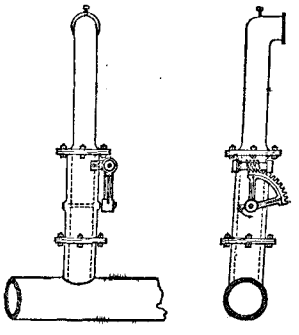


Fig. 117. Blast-pipe for each twyer of Rachette furnace.

Bar-iron made from No. II. in the charcoal-finery contained 2·95% of copper and 0·011% of sulphur.

Lead-slags from the Sophienhütte, Lower Harz, have also been operated upon in a cupola at Königshütte, with a view to determine the degree of reducibility of the iron contained in them. The analytical results obtained by Streng, March, 1866, are as follow :—

COMPOSITION OF THE LEAD-SLAG.

Silica	18·15
Alumina	0·22
Lime	4·55
Magnesia	1·63
Baryta	2·86
Protoxide of iron	48·96
Protoxide of copper (CuO)	1·97
Protoxide of lead	0·15
Protoxide of manganese	3·23
Zinc	1·89
Sulphur	5·88
	89·49

The analysis is so recorded,[2] except the sum total which is given as 99·49. The error is most probably typographical, and should fall upon the alumina or lime. Traces of arsenic, antimony, selenium, thallium, indium, strontium, and silver were also detected, no doubt chiefly by means of the spectroscope.

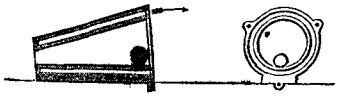


Fig. 118. Longitudinal section and end elevation of twyer of Rachette furnace.

[2] Berg- und hüttenm. Zeit. 1867, p. 61.

The cast-iron produced contained the following ingredients, according to Dr. Hilgenberg :—

CAST-IRON FROM LEAD-SLAGS CONTAINED PER CENT.

Sulphur	2·17
Silicon	0·08
Carbon	1·20
Phosphorus	0·18
Copper	1·40

The slags formed along with the cast-iron were only partially analysed, and the results are as under :—

	Per cent.	
	Glassy.	Stony.
Silica	34·90	33·20
Protoxide of iron	6·30 (4·90 iron)	5·00 (3·90 iron)
Protoxide of copper (CuO)	0·22 (0·18 copper)	0·45 (0·36 copper)

The cast-iron yielded by the slags above mentioned has been tried as a reducing agent in *Schlieg*[3]-smelting in the common *Schlieg*-smelting furnace with one twyer and in the Rachette furnace. The charge was as usual thus composed: 1 rost (=36 ctrs. dry, and from 36 to 40 ctrs. moist[4]) of *Schlieg* or fine ore, 4 ctrs. of iron, 1 ctr. of *Abstrich*, 1½ ctr. of first and last litharge, 9 barrows (containing each from 2·1 to 2·34 ctrs.) of regulus-slags (*i.e.* produced in regulus-smelting), and 7 barrows of slags from *Schlieg*-smelting. The lead and accompanying regulus produced in the two furnaces respectively have been analysed by Dr. Hilgenberg, and the results are as follow :—

FOREIGN MATTER IN THE LEAD, PER CENT.

	I.	II.
Antimony	0·767	0·778
Copper	0·153	0·217
Iron	0·004	0·008
Zinc	trace	0·011

I. From the common one-twyer furnace. II. From the Rachette furnace.

COMPOSITION OF THE REGULUS.

	I.	II.
Lead	16·22	29·15
Iron	52·40	40·69
Copper	2·26	3·71
Manganese, Zinc	0·67	1·41
Antimony	0·15	0·13
Sulphur	26·02	24·43
	97·72	99·52

[3] Also spelled Schliech.

[4] Die Oberharzer Hüttenprocesse, 2nd ed. Kerl, 1860, p. 680.

I. From the common one-twyer furnace. II. From the Rachette furnace. Thus, the regulus from the Rachette furnace contained much more lead and a little more copper than that from the one-twyer furnace.

Schlieg-Smelting with Lime in the Rachette Furnace.

The smelting-mixture which has been found to be best, and to give satisfactory results, is thus composed:—

100 ctrs. of *Schlieg*, ⅛ agglutinated by admixture with 4% of lime (36 ctrs.) and 72 ctrs. unagglutinated.
90 ctrs. of Lower Harz copper ore slags.
75 ctrs. of *Schlieg*-slags.
4 to 5 ctrs. of impure litharge.

The pressure of the blast was equal to a column of mercury of from 9 to 10 lines, and the diameter of the blast-pipes at the muzzle was $1\frac{3}{4}''$. Under these conditions, during a campaign 142·96 ctrs. of *Schlieg* were daily smelted: the products were 87 ctrs. of lead and 69 ctrs. of lead-regulus, and the consumption of fuel was 65 ctrs. 21 lbs. of coke; or for 100 ctrs. of *Schlieg*, 60·91 ctrs. of lead, 48 ctrs. of regulus, and 45·61 ctrs. of coke. The smelting-mixture was charged in horizontal layers as in charging an iron-smelting blast-furnace. In the first trials the reducing action was too powerful and iron attached itself to the hearth.

Alleged advantages of Schlieg-smelting with copper ore slags in the Rachette furnace over that in one of the usual Schliegöfen or blast-furnaces with a single twyer:—

1. Production twice or twice and a half larger.
2. Greater yield of lead.
3. Formation of regulus richer in copper but poorer in lead.
4. Formation of slags less rich in lead.
5. Production of less fume.
6. Considerable pecuniary gain in avoiding the use of cast-iron as a reducing agent, and in extracting nearly the whole of the silver and copper from the Lower Harz copper-slags; which metals are concentrated in the reduced lead and accompanying lead-regulus respectively.
7. Saving in wages.
8. Longer duration of a smelting campaign.

It is necessary to state that the lead produced in these two kinds of furnaces did not differ notably in the proportion of foreign matter, though in that respect the lead from the Rachette furnace was slightly superior to the other.

FOREIGN MATTER, PER CENT.

	I.	II.
Copper	0·2850	0·2240
Iron	0·0031	0·0045
Antimony	0·4420	0·6970
Sulphur	trace	trace

I. Lead from the Rachette furnace. II. Lead from the common *Schliegofen*. Both samples of lead were produced September 15th, 1866. The analyses were made by C. Ey.

The regulus produced in the two furnaces respectively from the same kind of *Schlieg* or fine ore August 27th, 1866, had, according to Ey, the following composition :—

COMPOSITION OF LEAD-REGULUS.

	I.	II.
Iron	55·90	46·63
Copper	3·33	2·37
Lead	10·88	21·65
Antimony } Arsenic }	0·27	0·17
Zinc	1·13	0·81
Sulphur	26·67	26·57
	98·18	98·20

I. Regulus from the Rachette furnace: it contained 2·5 quint of silver per centner. It has been found that the regulus from this furnace is on the average about 1·6% or 1·7% richer in copper than the common *Schliegstein* or lead-regulus from the usual mode of smelting, which is owing to the use of Lower Harz slags. II. Regulus from the common *Schliegofen*.

It is remarked that the fact of the regulus from the Rachette furnace containing from 8% to 10% less lead than that from the other furnace, gives hope of the possibility of avoiding the chief evil of the Upper Harz process of reduction by iron, namely, the waste of time and costliness of the repeated roastings and smeltings of the regulus. Thus, it has already been proved by experiments on a large scale at Oker, that by roasting such a regulus as that above mentioned from the Rachette furnace in kilns, there is an important saving of fuel, and the sulphurous acid evolved during the process may be advantageously applied to the manufacture of sulphuric acid.

One of the most noteworthy results of smelting *Schlieg* in the Rachette furnace is alleged to be the *cleanness* of the slag produced with respect to lead and silver. While the ordinary slags from the one-twyer furnace contain from 3 to 5 lbs. per centner (of 100 lbs. = 50 kilogrammes) of lead and from 0·12 to 0·19 quint (1 quint = 5 grammes) of silver per centner, the slags from the Rachette furnace contain on the average 0·9 lb. of lead and 0·06 quint of silver per centner, and occasionally only 0·5 lb. of lead and 0·03 quint of silver

per centner. The composition of these slags has been found to be as follows :—

COMPOSITION OF SLAGS FROM THE RACHETTE FURNACE.

	I.		II.	
Silica	45·1		41·06	
Protoxide of iron	33·4		38·37	
Protoxide of lead	1·02	(0·95 lead)	0·88	(0·82 lead)
Alumina	8·4		7·28	
Lime	7·8		7·58	
Magnesia	0·9		0·93	
Copper, Antimony	trace		trace	
Oxide of zinc, Protoxide of manganese	3·4		1·60	
Alkalies	—		—	
Loss	—		—	
	100·02		97·70	

I. Analysis by Kerl of the slag produced August 14th, 1866. It contained 1 quint of silver per centner.

II. Analysis by Dr. Hilgenberg of average sample of the slags from August 15th to September 12th, 1866.

For the sake of comparison are here inserted analyses of the ordinary slags produced in smelting *Schlieg* in the one-twyer furnace.

	I.	II.	III.
Silica	43·13	41·90	41·52
Alumina	4·76	4·09	10·37
Lime	5·77	11·64	5·22
Magnesia	0·78	1·36	0·16
Protoxide of iron	37·72	34·82	35·28
Protoxide of manganese	0·30	—	—
Protoxide of lead	6·32	2·40	6·59
Oxide of zinc	—	2·40	—
Potash	—	0·60	0·49
	98·78	99·21	99·63

I. From the Clausthal Hütte. II. From the Altenau Hütte. III. From the Lautenthal Hütte. The silver per centner in I. (and II.?) is given at from 0·12 to 0·15 quint.[5] More slags are produced in the Rachette furnace than in the other; but they are, as previously mentioned, poorer in lead.

The fact of a smaller quantity of fume being formed in the Rachette furnace than in the other is attributed to the diminished velocity of the upward gaseous current and the lower pressure of the blast. In the ordinary smelting of *Schlieg* from 4% to 5% of fume is produced,

[5] It is not clearly expressed whether the reference is to No. I. only or to Nos. I. and II.

while in the Rachette furnace the fume amounted to from 0·5% to 0·9% of the *Schlieg* smelted (?).

With regard to saving in wages, the Rachette furnace requires twice as many men as the other furnace, but its produce is more than double that of the latter.

The Rachette furnace continued uninterruptedly in blast — in other words its campaign lasted—from July 17th to November 10th, 1866, *i.e.* 17 weeks; whereas in the ordinary furnaces it lasts only from 10 to 13 weeks.

The consumption of coke in the Rachette furnace is for 100 ctrs. of material smelted about 4 ctrs. greater than that in the ordinary furnace; and this is ascribed to the cooling effect of the water boshes of the hearth and of the water-twyers, as well as to that attending the reduction of iron from the slags.

The first Rachette furnace constructed at Lautenthal Smelting Works for smelting *Schlieg* in the manner above described, namely, substituting Lower Harz copper-slags for granulated cast-iron, was blown-in December 4th, 1866, and blown-out June 4th, 1867, so that it had been 183 days in blast. A detailed account of the work done during that period has been published by the manager, E. Strauch,[6] of which the chief items are here presented on account of the novelty of the results.

Were smelted:[7]—

7,810	ctrs. of	*Schlieg* agglutinated with 3% of lime.
16,773	,,	unagglutinated *Schlieg*.
24,583	ctrs. of	*Schlieg*.

Were mixed with this Schlieg:—

8,515	ctrs. of	slags from old *Schlieg*-smelting.
1,655	,,	old slags from first smelting of lead-regulus.
6,259	,,	*Schlieg*-slags from the Rachette furnace of the same campaign.
25,821	,,	Lower Harz copper-slags.
450	,,	hearth.
954	,,	*Vorschläge* (impure litharge).
12	,,	*yellow Abstrich*.
68,249	ctrs.	total material for smelting.

Produced therefrom:—

69,487 ctrs.	15,294	ctrs. of	lead (as reduced. *Werkblei*.)
	13,728	,,	lead-regulus.
	259	,,	fume.
	19	,,	furnace accretions. (*Ofenbruch*.)
	32,649	,,	clean slags.
	7,438	,,	unclean slags.
Fuel consumed	8,892	ctrs.	of coke.
	68½	,,	charcoal.

[6] Berg- und hüttenm. Zeit. 1867, p. 323.

[7] 1 ctr. = 50 kilogrammes = 100 lbs.; 1 lb. = 10 loths; 1 loth = 10 quints.

Daily work:

Smelted:—134·33 ctrs. of *Schlieg* = 372·94 ctrs. of smelting-mixture.

Produced:—83·57 ctrs. of lead. (*Werkblei.*)
75·01 ,, lead-regulus.
1·415 ,, fume.
0·104 ,, furnace accretions. (*Ofenbruch.*)
218·5 ,, slags.

Consumed:—48·59 ctrs. of coke and 0·37 ctr. of charcoal (for preliminary warming of furnace and new hearth).

Per 100 centners of smelted dry *Schlieg:*

Produced:—62·21 ctrs. of lead. (*Werkblei.*)
55·81 ,, lead-regulus.
1·05 ,, fume.
0·077 ,, furnace accretions. (*Ofenbruch.*)
1·63 ,, slags.

Consumed:—36·17 ctrs. of coke, 0·2782 ctr. of charcoal, and 3 ctrs. of lime.

On the average during the whole campaign 1 lb. of coke was consumed for 7·675 lbs. of smelting-mixture or 2·764 lbs. of *Schlieg.*

PARTICULARS OF YIELD, INCLUSIVE OF ALL SLAGS ADDED.

	Silver.		Lead.		Copper.	
	lbs.	loths.	ctrs.	lbs.	ctrs.	lbs.
Delivered for Smelting:—						
In 24,583 ctrs. of *Schlieg*, of which 7,810 ctrs. were agglutinated with lime*	2,405	6·5	15,547	91	..	..
In 12 ctrs. of *Abstrich*, with 0·125 qt. (quint) silver and 86 lbs. lead, per ctr.	..	0·15	10	32	..	..
In 450 ctrs. of hearth, with 0·773 qt. silver and 66·3 lbs. lead, per ctr.	3	4·78	298	35	..	..
In 954 ctrs. *Vorschläger* (impure litharge), with 0·86 qt. silver and 82·6 lbs. lead, per ctr.	8	2·04	788	..	..	..
25,999 ctrs. of matters containing lead.						
Total, exclusive of slags	2,417	3·47	16,644	58	..	..
In the slags added:—						
42,250 ctrs.	42	2·3277	497	62	322	81
In 68,249 ctrs., total	2,459	5·79	17,142	20	322	81
Produced:—						
In 15,294 ctrs. of lead (*Werkblei*), with an average of 13·31346 qt. silver, per ctr.	2,036	1·6	15,273	64	..	..
In 13,728 ctrs. of lead-regulus with an average of 3·41 qt. silver, 9·99 lbs. lead, and 2·72 lbs. of copper, per ctr.	468	1·8	1,371	89	373	51
In 259 ctrs. of fume, with 7·5 qt. silver and 49 lbs. lead, per ctr.	19	4·25	126	91	..	..
In 19 ctrs. of *Ofenbruch*, with 2·75 qt. silver and 63 lbs. lead, per ctr.	..	5·225	11	97	..	..
Total, exclusive of slags	2,524	2·875	16,784	41	373	51
In 40,087 ctrs. of Rachette furnace slags, with 0·068 qt. silver and 1·23 lead, per ctr.	27	2·591	493	7	..	..
Total	2,551	5·466	17,277	48	373	51
Excess in products	91	9·67	135	28	50	70

* Average per ctr. 5·789 qt. silver and 63·25 lbs. lead.

For 100 parts by weight of silver computed to be present in the materials delivered for smelting, 103·8 parts were computed to be present in the products obtained; and similarly for 100 parts of lead in the former, 100·785 in the latter. The silver and lead were estimated to be distributed amongst these products as follows:—

	Silver per cent.	Lead per cent.
In the lead (*Werkblei*)	82·780	89·099
,, lead-regulus	19·030	8·000
,, lead-fume	0·790	0·740
,, *Ofenbruch*	0·021	0·070
,, slags	1·180	2·876
	103·801	100·785

In comparison with the old process of reduction by granulated cast-iron in a single-twyer blast-furnace, the yield of metal is notably raised, whilst the smelting-costs and the content of metal in the slags are lowered; on the other hand, the consumption of coke is increased in the proportion of about 10 ctrs. per 100 ctrs. of *Schlieg* smelted, for which reasons have been previously assigned.

At first the *Schlieg* or fine ore was smelted in the Rachette furnace with the usual addition of granulated cast-iron. The twyers being of the ordinary kind required to be frequently renewed. Nevertheless, there was saving of fuel, larger production, greater yield, less fume, and poorer slag. Water-twyers and water-blocks were adopted, by which the regular working of the furnace was secured and the smelting campaign was prolonged; but the consumption of fuel was increased and the regulus produced did not with respect to content of lead differ much from that obtained from the treatment of the same smelting-mixture in the common one-twyer blast-furnace.

It having been asserted that by heating in a coke-oven a mixture of powdered iron finery-slags and caking coal, a sort of coke was formed consisting in part of metallic iron, this was tried as a substitute for granulated cast-iron, Lower Harz copper-slags having been used in its preparation instead of iron finery-slags with a view to extract the copper and silver which they contained. Experiments, however, by Kerl on the small scale concerning the reduction of iron from such slags by the process in question gave unsatisfactory results.

The reader hardly requires to be cautioned not to regard what has been alleged concerning the merits of this furnace as sufficiently established. In the preceding pages of this volume we have seen melancholy examples of the want of accordance between the glowing statements of enthusiastic or interested inventors, and the results obtained by trials on the large scale under the direction of competent and disinterested persons. From what has been established in this country concerning the volatilization of lead from blast-furnaces, English smelters will be slow to accept statements so entirely opposed to their own experience as those above presented. Indeed,

the only effect of the publication of such extraordinary statements will be to render them more suspicious than they now are as to the accuracy and trustworthiness of columns of figures,—even in spite of the small fractions that may be introduced,—concerning the pecuniary advantages of newly proposed metallurgical schemes.

LEAD-SMELTING AT PRZIBRAM, BOHEMIA.

The ore is essentially argentiferous galena, which occurs in veins in sandstones, conglomerates, and schists of Lower Silurian age.[1] These lodes also yield cerussite (white-lead ore) and pyromorphite (green phosphate of lead); blende (sulphide of zinc); fahlore, poor in silver; vitreous-copper (Cu^2S) and copper-pyrites; bournonite; native silver; pyrargyrite (dark-red silver ore, $3AgS,SbS^3$); proustite (light-red silver ore, $3AgS,AsS^3$); stephanite (brittle sulphide of silver, 5 or 6 AgS,SbS^3); iron-pyrites, brown iron ore; antimonite (SbS^3); valentinite (SbO^3) and kermesite ($SbO^3,2SbS^3$), the last two very rarely; various antimonial lead ores, viz. boulangerite, etc.; and very seldom pitch-blende (uranium ore) and kupfernickel, which are almost confined to one lode (the Johanngang).

The vein-stuff consists mostly of calc-spar, brown-spar, dolomite, spathic iron ore, sulphate of baryta, and quartz. Spathic iron ore and quartz are met with in all the veins, calc-spar and brown-spar very frequently in the strongest, sulphate of baryta and dolomite more seldom. Generally calc-spar predominates in veins in greenstone, and quartz in veins in sandstone (Grauwacke). To the foregoing constituents of veins may be added detached fragments of sandstone and diorite, and clayey masses formed out of those fragments.

The same lodes of galena are not equally rich in silver continuously at the same depth. The proportion of silver increases with the depth, owing, it is stated, to intimate admixture of silver ores, especially fahlore and stephanite. The average content of silver in the galena, in what is designated the upper horizon, is from 4 to 6 loths per 100 lbs. of ore, *i.e.* in round numbers from 40 to 60 ozs. per ton, while in certain lodes at a greater depth ore has been met with containing from 20 to 25 loths per 100 lbs., *i.e.* from about 200 to 250 ozs. per ton.[2] The galena commonly also increases in quantity with the depth; and, what is interesting in a chemico-geological point of view, the more central thin layers are in many cases poorer in silver than the rest of the galena.

Argentiferous blende is frequently associated with the galena, and many assays of it from different veins and at different depths have shewn that when it is unaccompanied by galena, it contains merely a trace of silver, whereas if the two ores occur close together, the proportion of silver in the blende may amount to 8 or 10 loths per ctr.,

[1] See an elaborate paper by Grimm, entitled "Die Erzniederlage, bei Przibram in Böhmen." Berg- und hüttenmännisches Jahrbuch, 1856, 5. pp. 93–168.

[2] 1 ctr. = 100 lbs.; 1 lb. = 32 loths; 1 loth = 4 quents or quints, drams; 1 quint = 4 denars.

i.e. 80 to 100 ozs. per ton: on the average it contains from 1½ to 2 loths per ctr., *i.e.* from about 15 to 20 ozs. per ton: the brown blende is cadmiferous. Grimm has particularly investigated this important subject, and has assayed more than 100 specimens of blende from the most different points and depths of the Przibram veins; and such specimens only were selected with care for trial in which there was no visible trace of galena. The proportion of silver was found to vary in an extraordinary degree: while in some assays hardly a trace was detected, in the rest it amounted to several loths; many yielded from 4 to 5 loths, and one as much as 13 loths 3 quints per ctr. of 100 lbs.[3] As a rule the blende from lodes, where it was accompanied by galena rich in silver, contained most silver, though not a trace of galena could be seen in it. It is to be regretted that in these trials the blende was not chemically examined with regard to the presence of lead.[4]

ANALYSIS OF PRZIBRAM BLENDE.[5]

Zinc	65·12
Cadmium	1·73
Iron	1·62
Sulphur	31·53
	100·00

Analysis of the ores.—In 1859 A. Eschka analysed average assay samples of all the ores delivered at the Przibram Smelting Works in 1857, and his results are as follow:[6]—

COMPOSITION OF PRZIBRAM LEAD ORES.

	I.	II.	III.
Sulphide of lead	47·07	86·76	39·92
Sulphide of zinc	14·71	3·24	17·60
Sulphide of antimony (SbS^3)	1·68	2·28	1·04
Sulphide of silver	0·31	0·57	0·25
Bisulphide of iron	2·10	0·52	2·19
Carbonate of protoxide of iron	10·62	2·77	12·03
Carbonate of lime	1·75	0·75	1·75
Silica	17·05	2·95	19·10
Alumina with some manganese	3·70		4·90
	98·99	99·84	98·78
Metallic lead %	40·75	75·17	34·58
Metallic silver %	0·268	0·497	0·223

In each of these analyses traces of metallic copper were detected.

[3] Ueber die Verhüttung der Przibramer Erzgeschichte. Berg- und hüttenm. Jahrbuch, 1857, 7. p. 236. See also Beschreibung der Przibramer Schmelzprocesse; by Köller. Oesterreichische Zeitschrift für Berg- und Hüttenwesen, 1856, pp. 322–329, 341–349.

[4] An experienced British lead-smelter informs me, that he has met with several instances of blende and galena occurring in the same vein, in which the former was argentiferous and the latter not. But generally in this country when blende is associated with argentiferous galena, it contains only traces of silver.

[5] Berg- u. hüttenm. Jahrb. 1864, 13. p. 47.

[6] Ibid. p. 26.

I. Average sample of the total ores delivered in 1857.
II. Average sample of the rich ores ditto ditto.
III. Average sample of the poor ores ditto ditto.

The ores having been carefully assorted, according to the quality of their vein-stuff and mineral constituents are mixed on principles hitherto enunciated, so as to produce an uniform mixture well adapted for smelting; and from month to month it is found that the composition of the mixture is not subject to any remarkable variation: it contains on the average from 38% to 40% of lead, and from 7½ to 9 loths of silver per ctr. of ore, *i.e.* from 75 to 90 ozs. per ton. Lead-smelting at Przibram presents two particular points of interest, namely, the existence of about 20% of blende and 10% of silica in the mixture of ores treated. From olden times blende has been regarded by lead-smelters as their most mischievous enemy; and silica, when in such comparatively large quantity, is by no means a welcome guest. The blende cannot always be separated by hand, and accordingly special dressing operations, such as stamping, washing, etc., must be resorted to; and then even there must be limitation to its removal on account of the silver which it contains.

The ores may be divided into three classes, namely, pure argentiferous galena; galena associated with argentiferous blende and the other substances above enumerated; and argentiferous blende associated with other silver ores, etc., which being free from galena are designated "dry" ores. The question has arisen, whether it would be more profitable to smelt the first class by itself, and the other two classes together; and practical trials have been made with a view to its solution, which have led to the retention of the plan of smelting all three in admixture. There is a choice of evils: the third class in the absence of galena would require the addition of pyrites, in order to form a fusible regulus in which the silver might be collected; but pyrites could not be obtained in the locality at a sufficiently low cost for the purpose; hence, the alternative has been to throw aside blende and lose silver, or to smelt it in conjunction with galena and encounter the difficulty caused by the presence of a considerable quantity of zinc.

The ordinary process of lead-smelting consists of two operations, roasting and fusion in a blast-furnace with the addition of pig-iron and iron finery-slags. Roasting was formerly effected in heaps, and comprised three firings; but of late it has been performed in reverberatory furnaces or calciners, in a more satisfactory manner and at a less cost. The greatest length and breadth of the bed are 15′ and 11′ respectively. The charge is 20 ctrs., and the period of roasting 6 hours; and during the last hour the temperature is sufficiently raised to cause some clotting of the ore near the fire-bridge.[7]

The roasted ore is smelted in what the Germans designate a "half-high furnace" (*Halbhochofen*), which is trapezoidal in horizontal

[7] There was one so-called Kramer furnace in which the charge was only 6 ctrs.

section, and has the following dimensions: 2′ 2″ wide at the back or twyer-wall; 2′ at the fore-wall (inside measure); 3′ from fore to back-wall; 10′ 6″ high from the twyer to the mouth; and 1′ deep below the twyer. There is only one twyer, which inclines downwards about 2°, and the nose should be 8″ or 10″ long. The smelting-mixture is composed of 100 ctrs. of ore, from 6 to 8 ctrs. of pig-iron, from 10 to 12 ctrs. of lead products (*Abstrich*, cupellation hearth-bottoms, and the rich litharge which flows last, and other residua) according to what may be in stock, and from 36 to 48 ctrs. of iron finery-slags. The lead products vary as follow with respect to their content of lead and silver per centner:

	Lead. lbs.		Silver. loths (1 loth = ½ oz. troy).
Last rich litharge	82–88	.....	1¾–2½
Cupellation hearth-bottoms	62–65	.....	2–3
Abstrich (impure litharge)	80–86	.....	8–10
Furnace residua (Ofenkrätz)*	37–40	.....	2¼–3
Brasque	40–50	.....	4–5½ quints.
Fume			2½–3

* Mixture of slag and metal.

A smelting campaign (*i.e.* the period during which a furnace continues uninterruptedly at work from blowing-in to blowing-out) lasts from 18 to 24 days; and could not be protracted without great loss of fuel and metal, in consequence of the irregular widening of the shaft in the vicinity of the twyer and the formation of zinciferous accretions in large quantity. The products are slag from the fore-hearth infiltrated with lead-regulus, other slags, and fume, with of course the usual residua. Taking an average of 20 campaigns, each lasted 18 days, during which were smelted 752 ctrs. of ore, 227 ctrs. of "Krätz" (see note above), 125 ctrs. of leady products, 50 ctrs. of pig-iron and 343 ctrs. of iron finery-slags, the produce of furnace-lead being 226 ctrs. and the consumption of charcoal 380 tonnen (1 tonne = 10 cubic feet, and contains from 70 to 110 lbs. of fir and beech charcoal respectively).

In the preceding enumeration of the products of smelting, the omission of lead-regulus will excite attention; for, after studying the descriptions of the Tarnowitz and Upper Harz processes, the production of regulus composed largely of sulphide of iron might reasonably be expected. Yet in tapping there is no appearance of regulus, of which only traces can be detected in the slag from the cavity in front which receives the lead. Supposing, then, sulphide of iron to have been formed in the furnace, what has become of it? The answer is, it is diffused in the slags, not here and there in spots, but infiltrated throughout; and in these may often be seen enclosed particles of undecomposed and unmelted blende. It has been doubted whether the regulus is diffused mechanically in the slag, or exists chemically combined in the state of imaginary sulpho-silicate. That doubt has been removed by Mrázek, the results of whose investigation of the subject will be given further on.

While the smelting-mixture previously described contained on the average from 27 to 32 lbs. of lead and from 5 to 6 loths of silver per ctr., the resulting slag contained from 4½ to 7 lbs. of lead and 3 denars (1 quint = 4 denars) to 1½ quint of silver per ctr. It is evident that the intermingling of the regulus with the slag must cause notable loss both of silver and lead; and, accordingly, from time to time experiments have been made at the Przibram lead works with a view to remove that serious defect. The record of these experiments, which has been given by Grimm, may be studied with profit; and it appears to me nearly as important in metallurgical treatises to point out what has failed as what has succeeded, and especially to explain the causes of failure. I shall, therefore, present such of the results as I think most worthy of attention.

The iron-reduction process, as practised in the Upper Harz, at the Lautenthal Works in 1833, was tried with a mixture of galena and blende, containing from 61½ lbs. of lead, and 10 loths of silver per ctr. The smelting-mixture was thus composed: 100 ctrs. of ore, 12 ctrs. of leady products (cupellation-furnace-bottoms and litharge), 16 ctrs. of pig-iron, from 74 to 80 ctrs. of lead-slags, and from 36 to 40 ctrs. of iron finery-slags. The furnace was obliged to be blown out in the third shift, from "gobbing up," as may be inferred from the context. The tap or receiving cavity (*Vortiegel*) was put nearer the furnace, and the pig-iron was reduced from 16 to 12 ctrs., when the furnace worked better, though, indeed, unusual labour was required to clear out the accretions which were frequently forming. The campaign lasted 18 days: the slags contained from 2 to 3 quints of silver or more, and from 6 to 7 lbs. of lead per ctr.: there was no separation of regulus.

In other experiments were added 4 ctrs. of limestone per 100 ctrs. of ore, leady products up to 30 ctrs. or more, iron finery-slags from 48 to 54 ctrs., and in one instance 80 ctrs. of lead-slags. Occasionally regulus separated, and the slag retained only 1 quint of silver per ctr. The results were on the whole unfavourable; and the old process of roasting and smelting were resumed. Brunton's furnace, with a slowly revolving bed, was tried for roasting, and failed. At that time the conviction as to the pernicious influence of blende in smelting was so strong, that it was considered more profitable to leave wholly buried several thousand centners of blende containing more than 2 loths of silver per ctr. (*i.e.* about 20 ozs. to the ton) which had been delivered at the smelting works than smelt it along with the other ore.

In comparing experimental results like the foregoing with each other, which may have been obtained at different periods, or the results of one establishment with those of another, Grimm calls particular attention to a source of error which may greatly mislead. "I cannot," he writes, "suppress the remark, that at many smelting works, especially private ones, whether it be from carelessness, false shame, or conceit, the mischievous custom prevails of deceiving one's self. One plumes one's self on smelting with a small loss of metal

and a small consumption of fuel, and only too often, if the truth is spoken, the cause of the apparently better yield lies in the ore assay," or other circumstances.[8] Such observations would be more applicable to smelting works carried on by Governments with the funds of taxpayers at their disposal; for, as the balance-sheets of such establishments are published by authority, the managers who compile them must be sorely tempted to exhibit the results of their administration in the most favourable light. Balance-sheets, when honestly and accurately drawn up, will soon eradicate self-deception, false shame, or conceit.

In 1842 Grimm found that, by greatly reducing the proportion of lead-slags in the smelting-mixture for the ordinary process, the working condition of the furnace was much improved, regulus separated, and the yield increased. Whereas, previously never less than from 72 to 80 ctrs. of such slags had been smelted with every 100 ctrs. of ore, the quantity was then lowered first to 10 or 15 ctrs., and afterwards none were added. Hence Grimm arrived at the conclusion that there had been no separation of regulus in the ordinary process of smelting on account of the admixture of far too much lead-slag with the ore, that the whole of the regulus formed had remained diffused in the resulting slag, and that the failure of the trial at Przibram of the iron-reduction process of the Upper Harz might have been due to the same cause. In 1844 another attempt was made to introduce this process, and at the same time the furnace was somewhat modified: the tap or receiving cavity was constructed quite within the furnace, and the hearth was made correspondingly deep and large and nearer the twyer, in order to keep the hearth-bottom as far as possible hot, and so prevent the formation of accretions (*Ansätze*) from cooling. The smelting-mixture was composed of 100 ctrs. of ore, 10 ctrs. of pig-iron, from 4 to 5 ctrs. of limestone (which proved to be neither hurtful nor useful), and 70 ctrs. of iron finery-slags. The ore contained on the average from 40 to 62 lbs. of lead and from 7 to 8 loths of silver per ctr. When a portion of the ore had been smelted, the lead-regulus produced therefrom was roasted, and added to the remaining charges to the amount of 15 ctrs. per 100 ctrs. of ore, the proportion of iron finery-slags being at the same time reduced from 70 to 60 ctrs. Although the results were not completely satisfactory, yet they were sufficiently favourable when compared with those of the former trials, and when it is borne in mind that the ore treated was rich in blende. The working of the furnace was attended with many difficulties and required much labour, yet it nevertheless proceeded without derangement, and lead-regulus separated to the extent on the average of 30% of the smelting-charge.[9] In consequence of the sluggish flow of the slag there took place, though very rarely, that objectionable occurrence of the sudden outburst of regulus into the slag channel. Grimm considered that

[8] Op. cit. p. 245.

[9] Op. cit p. 248.

the foregoing results fully confirmed his opinion as to the reason of the previous failure at the Przibram Smelting Works of the iron-reduction process. The slags contained from 1 to 3 lbs. of lead and from 2 to 5 denars of silver (*i.e.* about 1 to 3 dwts.) per ctr., *i.e.* from about 1 to 3 ozs. per ton. The consumption of charcoal per 100 ctrs. of ore amounted to from 485 to 515 cubic feet. The general conclusions drawn by Grimm are as follow: the iron-reduction process is only applicable to the richer Przibram ores; it is more advantageous than the ordinary process only in the case of ores containing more than 65% of lead; and the Przibram ores will not be satisfactorily treated until the blende is separated, and subjected to some special process for the extraction both of its zinc and silver.

Grimm tried the experiment of roasting the ore in admixture with common salt (NaCl), and found that it tended to prevent clotting and quickened the process; but there soon followed a large deposition of lead and of chloride of silver in the fume-condensing chambers, on account of which the use of salt was wholly given up.

It is interesting to note that in 1846 Grimm experimented upon the practicability of so roasting the Przibram ores rich in blende and argentiferous blende by itself as to convert the zinc more or less into sulphate, which might be washed out with water. By roasting at a low temperature he succeeded in converting nearly the whole of the blende into sulphate of zinc; and the extraction of the zinc is rendered more perfect by the application of very dilute sulphuric acid. He computed that after subjecting argentiferous blende, containing 2 loths of silver per ctr., *i.e.* somewhat more than 20 ozs. per ton, to one of the usual zinc-extraction processes, and afterwards separating the silver from the residue in the retorts, the loss of this metal would amount to about 60% of the total in the blende.

Trials on the large scale in the direction of Grimm's experiments have been made at the Przibram Smelting Works; and in 1863 the result was reported to be unfavourable. The zinciferous ores were roasted and washed with dilute sulphuric acid; the insoluble residue containing lead and silver was smelted; white vitriol or sulphate of zinc was prepared from the solution and applied to the manufacture of sulphuric acid (by heat it is resolved into sulphurous acid, oxygen, and oxide of zinc); the residual oxide of zinc was used for the extraction of zinc by the ordinary method of reduction. The time required for solution was far too long, and there was much too soluble salt to be removed. The cost of wages and materials per centner of pure blende amounted to 5 fl. 54 kr., *i.e.* 11*s.* 9½*d.* The trials have been entirely given up, in the hope that hereafter the dressing of the poor ores may be so improved as to increase their content in lead and silver in a less costly manner than what has been described.[1]

In 1862 the poorer ores at Przibram contained on the average

[1] Berg- u. hüttenm. Zeit. 1864, p. 104, extracted from official reports by Neumann of Schemnitz, 1863.

40 lbs. of lead and 8 loths (about 4 ozs.) of silver per ctr., and constituted from $\frac{6}{7}$ to $\frac{7}{8}$ of the total ores delivered: they were smelted by the "so-called ordinary lead process." The remaining and richer part of the ore contained on the average in the same year about 74 lbs. of lead and 16 loths $3\frac{3}{4}$ quints of silver per ctr.: it was smelted in the raw or unroasted state by the iron-reduction process (*Niederschlagarbeit*).[2]

Spence's Process for the Treatment of Galena and Blende in intimate mixture.

A notice of this process may be appropriately inserted here, as supplementary to the foregoing account of Grimm's attempt to separate the zinc from such a mixture by means of dilute sulphuric acid. There occurs at the Mona and Parys mines in the Isle of Anglesey, a mineral called "Bluestone," which consists of the sulphides of lead and zinc so intimately mixed as to constitute a practically homogeneous substance, and to make it impossible to separate them by any method of dressing. More than one smelter has tried to deal with this ore in his furnaces, but in vain. Mr. Peter Spence of Manchester, the inventor of the well-known and successful process of manufacturing ammoniacal alum, has recently attacked this stubborn stuff and devised the following plan for its treatment, which he has patented.[3] The ore is reduced to powder and passed through a sieve of 60 holes to the linear inch. Hydrochloric acid, of sp. gr. 1·21, and therefore much stronger than the commercial acid, is stirred cold with the ore into a paste, which is then left to stand for some time, say a week. The sulphide of zinc is stated not to be acted upon by the acid, while the sulphide of lead is converted into chloride of lead, which is dissolved out by boiling water added in successive portions. The chloride of lead rapidly crystallizes, and the mother-liquor may be heated and used instead of fresh boiling water. The proportion of hydrochloric acid employed is determined by that of the galena present: if the lead in the ore amounts to 10%, the weight of acid should be 25% of that of the ore. The sulphide of zinc, thus freed from sulphide of lead, may be subjected to a zinc-extraction process, while the chloride of lead may either be applied to the manufacture of oxychloride of lead, or made to yield its lead in the metallic state.

Analytical data concerning Lead-smelting at Przibram.

We are indebted to Professor Mrázek, of the Imperial Mining Academy at Przibram, for valuable analytical investigations of products from the lead-smelting works in that locality.[4]

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[2] Berg- u. hüttenm. Jahrb. 1864, 13. p. 315.

[3] The title of the patent is "Separating Zinc from its Ores." A.D. 1867. April 3. No. 997.

[4] Berg- und hüttenm. Jahrbuch, 1866, 16. p. 392.

Roasted lead ores.—The substance analysed was an assay sample of the completely roasted and agglutinated product of the current roasting in 1866 in a reverberatory furnace of improved construction, narrower across the bed than the English reverberatory furnaces previously in use. The ore was first roasted, with frequent turning over, during 6 hours, and then during 2 hours at a high temperature, sufficient to render pasty what lay near the fire-bridge. The fracture of the product was dark-grey, and presented numerous glittering points of galena and blende, and white grains of quartz.

COMPOSITION OF ROASTED ORE.

Silica	21·43
Alumina	7·15
Lime	0·78
Magnesia	0·23
Protoxide of iron	4·78
Sesquioxide of iron	10·31
Protoxide of manganese	0·35
Oxide of zinc	22·62
Oxide of lead (PbO)	25·61
Antimonic acid (SbO^5)	1·50
Sulphuric acid	trace
Sulphur	3·85
Silver	0·128
	98·738

Hence it appears that the sulphuric acid of any metallic sulphates formed during the first stage of roasting had, during the after stage of agglutination at a higher temperature, been wholly evolved, for the most part doubtless having been displaced by silica. By the action of concentrated hydrochloric acid, all the sulphur was expelled as sulphuretted hydrogen, with separation of gelatinous silica, scarcely a trace of sulphuric acid remaining in the solution; and, therefore, it must have existed wholly in the residual sulphides, which, in the opinion of Mrázek, were "undoubtedly only sulphide of zinc and sulphide of lead, and for the most part at least still in their natural state of galena and blende mechanically mixed with the sintered silicated mass." It was not possible to determine experimentally how much galena and how much blende remained unaltered; but Mrázek approximately computed that the proportions were 4·2% of raw galena and 10% of raw blende.

The proportion of protoxide to sesquioxide of iron is nearly the same as in magnetic oxide of iron.

Mrázek directs attention to the similarity in composition of this roasted product with that which he obtained at Freiberg in 1865, and of which his analysis is given at p. 308 of this volume.

Lead-regulus.—An interesting series of analyses of products from the Przibram Smelting Works has been recently made by Balling, of the Mining Academy of that town; and in that series is the following

analysis (No. I.) of the lead-regulus produced in the ordinary process of lead-smelting at Przibram in 1863.[5] No. II. is by Klasek, of the regulus produced in 1852 in the same ordinary lead-smelting process at Przibram.[6]

COMPOSITION OF ORDINARY LEAD-REGULUS.

	I.		II.
Lead	9·385	.....	10·37
Iron	63·103	.....	62·78
Zinc	1·525		
Copper	0·771	.....	2·56
Nickel	0·365		
Cobalt	0·027		
Sulphur	21·866	.....	21·81
Antimony	1·107	.....	2·67
Arsenic	0·396	.....	..
Calcium	0·239	.....	..
Silver	0·097	.....	0·06
	98·881	.....	100·25

Assuming the lead, antimony, and zinc to be present in the state of PbS, SbS^3, and ZnS, respectively, the sulphur remaining after the abstraction of what is required to form these compounds suffices, as Mrázek points out, almost exactly to produce disulphide of iron (Fe^2S) with the iron present; and this also applies to Balling's analysis, which may be regarded as practically identical with that of Klasek.

Slag from ordinary lead-smelting at Przibram.—The composition of this slag has been elaborately investigated by Mrázek, especially with the view of ascertaining why the regulus, which is formed in the process, should only occasionally be separated and appear as a distinct product. In August, 1863, an average sample of the slags was prepared by taking a portion of slag during several days from each waggonful of slag as it left the furnace, and mixing and triturating the whole together after having carefully detached any adherent impurities, and every precaution was seemingly adopted to procure an accurately representative specimen for analysis. Although in the pieces of slag selected no included globules of metallic lead were visible, yet such globules were observed on close inspection, and by cutting with a knife; but of regulus not a particle could anywhere be detected. The slag was micro-crystalline in structure; its specific gravity was 3·75 at 21° C.; its hardness was considerable; but it had so little tenacity that pieces ½″ thick could easily be crushed in the hand. The following is the analysis of the slag as tabulated by Mrázek:—

[5] Berg- und hüttenm. Jahrbuch, 1867, 16. p. 409.
[6] Op. antea cit. 1864, 13. p. 360.

COMPOSITION OF LEAD-SLAG.

Silica	28·10
Alumina	5·00
Sesquioxide of iron	0·51
Protoxide of iron	47·14
Oxide of zinc	7·25
Protoxide of lead	2·38
Protoxide of copper (CuO)	0·31
Protoxide of nickel (NiO) / Protoxide of cobalt (CoO)	0·17
Protoxide of manganese (MnO)	trace
Lime	3·35
Magnesia	0·76
Silver	0·01*
Sulphur	2·71
Antimony	trace
Arsenic	trace
Phosphoric acid	2·52
	100.21

* Silver 3 ozs. 5 dwts. 8 grs. per ton.

No sulphuric acid existed in this slag, so that evidently it contained a notable quantity of metallic sulphide.

Mrázek tried in vain to determine by *wet* processes how the sulphur was distributed amongst the accompanying metals. Weak acids incapable of decomposing the silicates of the slag, certain solutions of salts, concentrated solution of cyanide of potassium, and alcoholic solution of iodine, were the agents which he employed for that purpose. He then attempted to separate the metallic sulphide, which the slag contained either mechanically diffused, or chemically combined, or in both states, by a method of fusion. He melted in a crucible an intimate mixture of 30 grammes of the slag, 50 of common glass (free from lead) and 30 of glass of borax, various precautions being observed, and obtained a distinct regulus composed as follows (No. I.) :—

COMPOSITION OF REGULUS.

	ARTIFICIAL REGULUS. I.		NATURAL REGULUS. II.
Iron	37·8	.....	63·103
Lead	12·8	.....	9·385
Zinc	11·0	.....	1·525
Copper	2·6	.....	0·771
Nickel with cobalt	1·5	.....	0·392
Silver	0·116	.....	0·097
Sulphur	26·94	.....	21·866
Antimony	1·1	.....	1·107
Arsenic	trace	.....	0·396
Sodium	3·2	.....	..
Calcium	..	.....	0·239
	97·056	.....	98·881

The sodium was clearly derived from the flux added, and is assumed by Mrázek to have replaced an equivalent proportion of iron, according to the equation $NaO+FeS=NaS+FeO$. This proportion is 3·9, which is therefore added to the iron found in the regulus, making a total of 41·7% of iron. Now this artificial regulus, as it may for the sake of distinction be designated, differs notably in composition from that of the natural regulus direct from the ore-furnace, and of which the composition is again presented in the second column above. The much smaller proportion of zinc in the latter is a striking, and probably the most important, point of difference.

On the supposition that, subject to the correction before mentioned of the replacement of sodium by an equivalent proportion of iron, the sulphur in the slag represents intermingled regulus according to the preceding analysis, then Mrázek deduces the following as the composition of the slag :—

COMPOSITION OF SLAG.

I. Oxygen compounds.

Silica	28·10		
Alumina	5·00		
Sesquioxide of iron	0·51		
Protoxide of iron	41·75		
Oxide of zinc	5·87		
Protoxide of lead	1·00		
Protoxide of manganese	trace		
Lime	3·35		
Magnesia	0·76		
Phosphoric acid	2·52		
		.....	88·86

II. Sulphur compounds.

Sulphur	2·71		
Antimony	0·11		
Arsenic	trace		
Iron	4·19		
Lead	1·29		
Zinc	1·11		
Copper	0·26		
Nickel and cobalt	0·15		
Silver	0·012		
	9·832		
Loss (*Abgang*) of the regulus analysis	0·298		
		.....	10·13
			98·99

The artificial regulus separated by the process of fusion previously mentioned contains practically the whole of the copper, nickel, cobalt, antimony, and silver originally existing in the slag, as will clearly appear from the following tabular statement :—

By direct analysis per cent.	Silver.	Copper.	Nickel and Cobalt.	Antimony.
In the artificial regulus	0·012	0·26	0·15	0·11
In the slag	0·010	0·25	0·13	trace

Hence it may be concluded that the metallic sulphide in the slag is essentially the holder, so to speak, of the silver and the associated metals here specified, *i.e.* provided that, as in the slag under consideration, there is not sufficient arsenic to form *Speise* in appreciable quantity.

After separation of the artificial regulus, there remained in the state of oxidized compounds in the resulting slag 41% of the total lead and 81% of the total zinc, so that 59% of the total lead and only 19% of the total zinc occurred in the regulus. This is precisely what might have been anticipated from a consideration of the affinity of lead and zinc for sulphur and oxygen respectively. The antimony, arsenic, nickel, cobalt, and a portion of iron are properly regarded by Mrázek as speise-forming elements; and, accordingly, he eliminates them from the regulus, and computes that the slag contains 0·3% and the artificial regulus 3% of speise. Admitting the copper in the artificial regulus to exist as disulphide (Cu^2S), and the zinc, lead, and silver as monosulphides (RS), the remaining iron and sulphur are in the proportion $Fe^8 : S^7$, which corresponds to the formula $6FeS+Fe^2S$. The composition of this regulus may be represented by the formula $20RS+3R^2S$, in the latter member of which is included the copper as disulphide.

The source of the phosphoric acid in the slag is, doubtless, with reason, ascribed by Mrázek to the iron-slags, which form so large a proportion of the charge in the ordinary lead-smelting process at Przibram, and of which part is produced in charcoal-fineries and part in puddling-furnaces. It is inferred, though not on unexceptionable grounds, that this acid is combined according to the formula RO or $R^2O^3+PO^5$. Whether this inference be true or false is not very material in considering the constitution of the slag in question, which is certainly tribasic, and may be expressed by the formula $5(3RO,SiO^3)+Al^2O^3,SiO^3$.

On the retention of the regulus in the slag.—Admitting the correctness of Mrázek's analysis of the slag, it is certain that a notable quantity of sulphur existed in that slag in the state of sulphide, but it may be asked whether this sulphide represents regulus mechanically disseminated, or whether it occurs chemically combined as sulphosilicate or oxysulphide. Mrázek has carefully considered these questions, and, as it seems to me, rightly decided in favour of the first, or that of intermingled regulus. The sulphosilicate hypothesis is shown to be wholly groundless; and the oxysulphide hypothesis equally untenable. A microscopic examination of the slag might possibly have revealed the presence of regulus in particles too minute for detection with the naked eye; but no such examination, it is to be regretted, appears to have been made.

The specific gravity at 21° C. of the slag, artificial regulus and natural regulus, was, respectively, 3·75, 5·23, and 5·66; and this difference in density between the slag and regulus is sufficient to cause the subsidence and separation of the latter from the former, provided the *whole* mass be thoroughly melted and continue so for

a short time. But supposing the regulus to be much less fusible than, and to be finely disseminated through, the slag, then it is easy to conceive that, while it would gradually subside, yet its particles might be too viscous, or in other words not sufficiently liquid, to enable them to coalesce and form a distinct layer at the bottom. Now, it is well known that the fusibility of a regulus is lessened by the presence of sulphide of zinc; and this sulphide has in consequence occasioned not a little inconvenience and difficulty in various metallurgical operations, of which a striking instance has been given in the description of copper-smelting at Åtvidaberg.[7] On the other hand, the fusibility of a slag is lessened by its containing oxide of zinc in combination with silica; and, *cæteris paribus*, the less a slag is fusible, the less perfect will be the separation of regulus from it, that is, supposing the temperature of the furnace not to be increased beyond what is usual. Moreover, the degree of liquidity of a slag even when completely molten, is a potent and important element in the consideration of this subject, with respect both to slag and regulus; and what has been previously advanced concerning the silicate as well as the sulphide of zinc indicates that a slag containing oxide of zinc and a regulus containing sulphide of zinc in notable proportion would have their liquidity diminished, or, what is equivalent, their viscosity increased. Silicate of zinc of whatever formula requires a very high temperature for its fusion, but melts easily and becomes thinly liquid on the addition of boracic acid.[8] The artificial regulus above referred to was, it will be borne in mind, separated by heating the slag in admixture with glass and boracic acid; but in this case the separation of regulus cannot be wholly ascribed to the increased liquidity of the molten mass, because the composition of this regulus differed much from what has been designated the natural regulus, the former containing 37·8% of iron and 11% of zinc, and the latter 63·1% of iron and only 1·5% of zinc. In order conclusively to determine the cause or causes of the retention of regulus under ordinary circumstances in the Przibram lead-slag, further investigation is required, microscopical as well as chemical. There is good reason for believing that the skilful use of the microscope will elucidate many obscure and interesting points connected with metallurgical products and operations; and to Mr. Sorby, of Sheffield, much credit is due for having applied that instrument with excellent effect in the examination of iron and steel, as well as in various investigations relating to chemical geology.

SMELTING OF OXIDIZED ORES AND PRODUCTS.

Common or North of England Slag-Hearth.

From the study of the various processes of lead-smelting which have been described in the preceding part of this volume, it will have been remarked, that in all the slags formed in those processes

[7] See first part of this work.

[8] Ibid.

lead exists in an oxidized state, and in some cases in very large proportion, *e.g.*, the grey-slag. The production of lead-regulus is an evil which should always be avoided whenever it is practicable, and this can only be attained in the air-reduction process, by producing slag containing oxide of lead in considerable quantity. Hence it becomes necessary to extract from such slag as much lead as possible consistently with economy. With this object it is subjected to treatment precisely similar in principle to that of calcined galeniferous ores in the blast-furnace, or that of the slag of the Bleiberg or Cornish processes in the reverberatory furnace. The principle is deoxidation, either exclusively by carbonaceous matter, or by the combined action of such matter and iron.

The object of this hearth is the extraction of the lead contained in the rich *grey-slags* of the ore-hearth, or in other matters, such as furnace residua, in which lead is present in notable quantity in an oxidized state. The hearth is a small blast-furnace, and although it varies somewhat in dimensions, and in minor details of construction at different works, yet everywhere it is substantially the same. I have drawings of these hearths from several smelting works in the north of England, and they are all so similar that it would serve no useful purpose to present engravings of them. I have selected for description and illustration a comparatively recent slag-hearth, which will amply suffice.[1] The slag-hearth belongs to the same class of furnaces as the *Krummofen* of the Germans, the *Fourneau à manche*[2] of the French, and the *Pava* of the Spaniards.

Description of the slag-hearth.—The annexed woodcuts (119 to 125 inclusive) are from drawings of a slag-hearth at the Keld Head Mining Company's Smelting Works near Leyburn, Wensleydale, Yorkshire, which were made expressly for this volume by my friend and former student, Mr. William Weston; and for the following account I am also indebted to the same friend, who, at my request, has particularly observed and described the process.

The slag-hearth is a small rectangular blast-furnace with one twyer. It is made of fire-brick and cast-iron encased in common brickwork or other material except in front. The outer casing is prolonged upwards forming a chimney, which at the top is connected with a long flue or other arrangement suitable for the condensation and collection of lead-fume.

a. Interior of the furnace. *b b.* Lining of fire-brick.

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[1] The slag-hearth will be found described in Westgarth Forster's 'Treatise on a section of the Strata from Newcastle-upon-Tyne to the Mountain of Cross Fell in Cumberland,' 8vo. 1821; and in Pattinson's paper on Lead-Smelting in Northumberland, Cumberland, and Durham, contained in the Trans. of the Nat. Hist. Soc. of Northumberland, Durham, and Newcastle-upon-Tyne, 4to. 1832.

[2] Petitgand states that this term is derived from the Spanish *manchia*, or leather sleeve connecting the bellows with the blast-pipe; and so the name of a particular part of the blowing apparatus has been applied to the entire furnace. In the north-east of Spain they are known under the name of *Manchia*, and in the south of Spain under that of *Pava*.

c c. Outer casing of common brick or other material.

d. Plate of cast-iron forming the front, named *fore-stone.*

e. Plate of cast-iron forming the back of the furnace below the twyer.

f f. Blocks of cast-iron, named *bearers*, carrying the side-walls of the furnace.

g. Plate of cast-iron, named *bed-plate*, forming the bottom of the furnace and sloping downwards and forwards.

h. Open space between the lower edge of the *fore-stone* and the *bed-plate.*

i i. Trough of cast-iron, named *lead-trough*, divided by an iron partition into two unequal parts, the larger immediately in front and the smaller one on the left between the letters *i i:* there is a hole at the bottom of the partition, through which molten metal may flow from one part into the other: the trough is cast in one piece.

k. Trough of brickwork, named *slag-pit.*

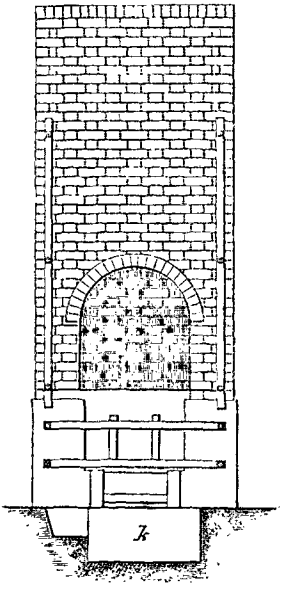


Fig. 119. Front elevation.

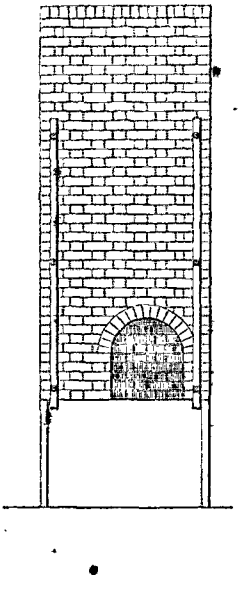


Fig. 120. Left side elevation.

The shaft above the furnace has by mistake been represented in the woodcuts as higher than it actually is; and it should be shown as arched over at the top and not as flat. But these differences are quite immaterial.

The outer brickwork below corresponding to the hearth is supported by cast-iron plates with suitable bracings of wrought-iron. The twyer passes through the cast-iron plate, fig. 122; and at the top of fig. 122 is shown the arched opening connecting the chimney of the

hearth with the fume-condensing arrangement. Above the hearth in front is an open space arched at the top, as shown in fig. 119; and there is also a similar but smaller opening on the left, as shown in fig. 120. The position of the twyer is shown in figs. 123, 125.

The *bed-plate* is covered with a layer of hard-burnt and coarsely-sifted coal ashes to within about 1″ below the nozzle of the twyer, forming the ash-bottom, which is made to slope towards the lower edge of the *fore-stone*. The space in front of the ash-bottom between the *bearers* is plastered up with clay. This ash-bottom acts as a filter by means of which the molten slag and lead which, in the process of smelting, fall to the bottom of the hearth, are separated from each other, the slag running out over the ash-bottom through openings made in the clay stopping under the lower edge of the *fore-stone*, while the lead percolates through the ash-bottom to the *bed-plate* and

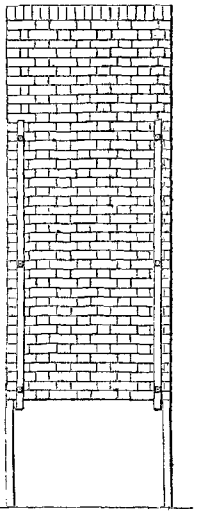


Fig. 121. Right side elevation.

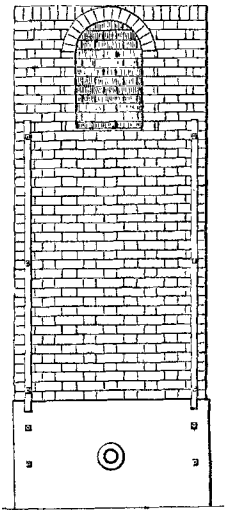


Fig. 122. Back elevation.

runs down into the *lead-trough* in front. The larger division of the lead-trough is filled with spongy cinders, which likewise act the part of a filter, the slag flowing over the top into the slag-pit, previously filled with water, while the lead runs through and finds its way to the bottom, where it is laded out from the smaller division on the left.

The products of smelting in the slag-hearth are *slag-lead* and vitreous *black-slag* which is thrown away. The fuel is coke and peat. The hearth is worked by two men, a smelter or charge-man as he is termed, who has charge of the hearth, and a labourer who supplies the material to be smelted, including fuel, and removes the *slag-lead* and *black-slag* produced. A shift lasts about 8 hours, during 6 of which the blast is uninterruptedly continued, while 2 hours are devoted to the preparation of the furnace and emptying it at the close

of a shift. This preparation consists in "stubbing out" from the sides all the slaggy matter left adhering to them from the preceding shift, and "stemming up" with clay those parts of the furnace much burnt in: the detached slaggy matter is put aside to be re-smelted.

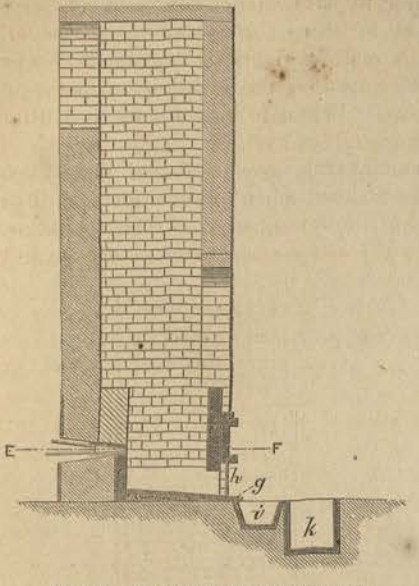


Fig. 123. Vertical section on the line A B, fig. 125.

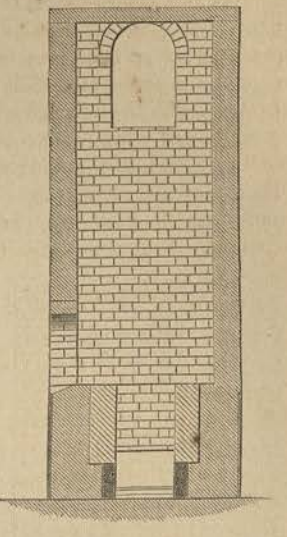


Fig. 124. Vertical section on the line C D, fig. 125.

In lighting the hearth, "peats" (*i.e.* the usual rectangular pieces of peat) are put in, a little burning coal is placed in front of the twyer, and the blast is then let on, after which the whole becomes quickly ignited. About 1 cwt. of coke is now added, and while the fire is burning up the men sharpen their stubbing-tools to have them ready for the next shift. With more coke is introduced a little of the *brouse* left from the previous shift (agglomerated semi-reduced lumps of ore). From the beginning of the shift to this stage 1½ or 2 hours are consumed. As the hearth becomes hotter, *grey-slag* mixed with a little *brouse* and *black slag* is thrown in, and when the smelter, judging from the time which has elapsed since he began to charge with smelting materials, thinks that slag has begun to melt, he makes a hole in the centre of the stopping under the lower edge of the fore-stone; for which purpose he uses a bar of iron pointed

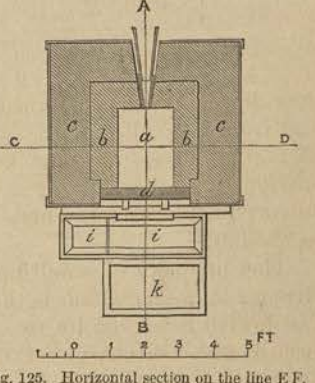


Fig. 125. Horizontal section on the line E F, fig. 123.

and curved upwards at one end. The slag flows out through this hole, and the hearth being now in full working order, fuel and material are added as required, care being taken to keep the blast as uniformly distributed as possible.

When the furnace is working to one side or burning too freely, less coke in proportion to material is added. As the *slag-pit* fills it is emptied; but should the hearth not be working regularly and the smelter suspect any lead to have gone over with the slag, the latter is put a side to be worked over again when it may be convenient to mix it with material to be smelted.

To end the shift no more material is charged, and the blast is kept on for about 20 minutes or ½ hour, after which it is shut off and the clay-stopping in front of the ash-bed is removed. The smelter then works out the ashes on the *bed-plate* with a poker, and as much of the adherent slaggy matter as practicable, which is preserved for re-smelting in the next shift under the name of *slag-hearth brouse*. A few bucketfuls of water are thrown into the hearth in order to put out the fire and cool the interior preparatory for stubbing at the ensuing shift.

The use of iron slag (basic silicate of protoxide of iron) is very beneficial when the *grey-slag* is at all "stiff and short." The material to be smelted should not contain more than 35% of lead (by dry assay); and if richer it should be mixed with *black-slag* or other material poor in lead. When different kinds of material are so mixed, it is stated that the furnace works better and the result is more satisfactory.

RESULTS OBTAINED DURING ONE SHIFT AT THE SLAG-HEARTH OF THE KELD HEAD MINING COMPANY, WENSLEYDALE.

Weight of Brouse at the commencement of the Shift.	Weight of Brouse at the close of the Shift.	Weight of Grey-Slag smelted during the Shift.	Quantity of Ore from which the Grey-Slag was produced.	Weight of Lead obtained from the Ore producing the Grey-Slag.
cwts. qrs. lbs.	cwts. qrs. lbs.	cwts. qrs. lbs.	Tons. cwts.	Tons. cwts. qrs.
5 3 0	7 2 0	45 0 21	32 0	23 5 0

Produced		Percentage yield of Lead.		Fuel consumed.			Cost of Peats.
Lead.	Black-Slag.	On the Grey-Slag.	On the Ore.	Coke.	Cost of Coke.	Peats.	
cwts. qrs. lbs.	cwts. qrs. lbs.			cwts. qrs. lbs.	*s.* *d.*	Bushels.	*s.* *d.*
9 0 0	24 0 0	19·91	1·40	7 2 10	6 11	4	1 5 per ton of lead produced

The advantages of the slag-hearth above described over the old form of North of England slag-hearth, previously in use at the Keld Head Mining Company's Works, are *alleged* to be as follow:—

1. Larger yield of lead.
2. Production of a cleaner black-slag.

I have received no analytical evidence in proof of the latter statement.

A comparative trial was made in the two kinds of hearth with the *same heap of grey-slag*, and was continued during four shifts at each, the same workmen being employed.

Old hearth.—45 cwts. of *grey-slag* were passed through in 6 hours with a consumption of 9 cwts. of coke, producing 8 cwts. of lead.

New hearth.—80 cwts. of *grey-slag* were passed through in 6 hours with a consumption of 9 cwts. of coke, producing 18 cwts. of lead.

The quantity of slag smelted in the slag-hearth in a given time varies with the quality of the slag.

Mr. Pattinson published in 1832 the following results of the North of England slag-hearth. The shift lasted from 14 to 16 hours, and during that time the produce of lead varied from 10 to 21 cwts., according to the nature of the slags. From 15 to 18 cwts. of coke were required to furnish 21 cwts. of lead. In large transactions it was usual to reckon that for 13 parts by weight of common or furnace lead obtained there would be 1 part of slag-lead.[3]

Small Slag-hearths in Spain.—They are described by Petitgand as built of stones, strongly supported with massive buttresses for want of iron bracings, and having an internal lining of large bricks of *launa*, a kind of refractory clay derived from decomposed talcose schists. The hearth-bottom is made of a mixture of about $\frac{2}{3}$ of this clay and $\frac{1}{3}$ of pounded charcoal or coke, and from it there proceeds a channel to a small circular cavity outside, hollowed out in the ground against the furnace in the angle of the inclined plane upon which the slag runs out. They are represented as rectangular in horizontal section. The most usual dimensions are as follow: height from the hearth-bottom to the mouth, 0^m 85 to 1^m 30 (2′ 9″ to 4′ 3″); from back to front, 0^m 84 to 0^m 90 (2′ 9″ to 2′ $11\frac{1}{2}$″); and width, 0^m 70 to 0^m 74 (2′ $3\frac{1}{2}$″ to 2′ 5″). There is one twyer made of clay. The blast is produced by double bellows of leather, which are worked either by man or mule-power, and deliver from 4 to 5 cubic metres (141 to 176 cubic feet) of air per minute. The furnace complete costs about 1000 reals (say 10*l.* 10*s.*) exclusive of bellows, which cost from 5000 to 6000 reals (say from 52*l.* to 63*l.*). The smelting-charge consists of rich slags (*crasses blanches*), old slags (in the proportion of $\frac{2}{3}$ of the latter to less than $\frac{1}{3}$ of the former), skimmings, and all other plumbiferous residua from previous operations. From 120 to 150 Spanish quintals (from about 108 to 135 cwts.) of rich slags are passed through in 24 hours with a consumption of from 20 to 24 quintals (from about 18 to 22 cwts.) of coke. The resulting slag is stated not to contain more than from 1% to $1\frac{1}{2}$% of lead, though occasionally there is considerable volatilization. The yield is from 15% to 18% with a consumption $1\frac{1}{4}$ part by weight of fuel for 1 of metal.

[3] Trans. of the Nat. Hist. Soc. of Northumberland, Durham, and Newcastle-upon-Tyne, 1832, 2. p. 165.

The special costs on 100 kil. of lead are given as 12·022 francs, *i.e.* about 5*l.* per ton, while the special costs per ton of lead obtained in smelting rich slags (*crasses*) in the Carthagena furnace are stated to be about 3*l.* 5*s.* 7*d.*

THE SPANISH SLAG-HEARTH.

The Spanish slag-hearth is a blast-furnace which, according to M. Petitgand[1] was invented by a Frenchman, M. Roux de Freycinet, manager of the Smelting Works of San Isodoro, in the bay of Escombreras in the south of Spain.[2] It was specially designed for the treatment of Roman lead-slags. It is circular in plan, with a sloping bottom. It is slight in construction with respect to brickwork, consisting only of single brick, *i.e.* 9″ in thickness; and this M. Petitgand regards as advantageous. It must be built of proper arch fire-bricks, so laid as to break joint with each other in the successive courses. The original furnaces in Spain of this description had no breast-pan of cast-iron like that to be presently described.

The Spanish slag-hearth has during recent years been thoroughly tried at various lead-smelting works in England and Wales, and has been abandoned by some of our largest and most experienced lead-smelters, who have expressed to me their opinion of it in language far from respectful. Thus, one smelter friend calls it a "beastly thing." It is affirmed that the escape of lead from it by volatilization is very considerable. It is stated to be very well suited for expeditiously smelting poor and easily fusible slags, like some of those of Derbyshire, but not for the treatment of such rich slag as is produced in the Flintshire furnace. I have seen it in operation in several locali-

[1] Exploitation et Traitement des Plombs dans le Midi de l'Espagne. Par M. Petitgand. Extrait de la Revue Universelle, 1861, p. 94.

[2] The smelting of old lead-slags within a comparatively recent period has been profitably conducted both in England and abroad. Bishop Watson, writing towards the end of the last century, states as follows:—"Near every smelting-house [in Derbyshire] there are thousands of tons of slag, which, when properly assayed, are found to yield from $\frac{1}{8}$th to $\frac{1}{10}$th of their weight of lead; though no person has yet discovered a method of extracting so much from them when smelted in large quantities; and indeed the smelters are so little able to obtain all the lead contained in them, that in many places they never attempt to extract any part of it: in some places, where they do attempt it, I have known the proprietor of the slag allow the smelters 20*s.* for every pig of lead they procured of the value of 38*s.*, besides furnishing them with fuel; and yet the men employed in such an unwholesome business, seldom made above 7*s.* a week of their labour." (Chemical Essays, 1782, 3. p. 293.) From a communication of the correspondent of the *Times*, for Greece, published October 27, 1865, the following extract is taken:—"Great expectations are formed of the sums that are to flow into the Treasury from the refuse of the old silver mines of Laurium, and from the discovery of new mines of lead and silver which are supposed to have escaped the notice of the ancients. A French capitalist, M. Roux, has purchased a considerable quantity of scoria of the ancient mines of Laurium from the municipality of the district, with the consent of the Greek Government. His experience, gained in a similar undertaking at Carthagena, and his prudent and liberal conduct in Attica, promise success in re-smelting the refuse of the old Athenian mines. But whether the inexperienced and penniless Athenians who propose to rival his enterprise will be able to pay the Greek Government hard cash for a concession of national mines, is at least doubtful."

ties, including Alport, near Bakewell, in Derbyshire, at the Smelting Works of Messrs. Barker and Rose; and it is this furnace that I have selected for description. I have much pleasure in acknowledging the assistance of Mr. Francis Barker in providing me with the drawings from which the annexed woodcuts have been prepared, nor can I omit to mention the names of Mr. Hornblower, and of the manager, Mr. Bennetts, to whom I am also indebted for information on the subject.

The problem is the extraction of lead from slags, in which the metal, as we have seen, exists for the most part in the state of silicate. Carbon and carbonic oxide are the reducing agents employed in this process, with the occasional addition of oxidized compounds of iron, like forge-cinder, to serve especially as flux. If the lead-slags contain sulphate of lead, this salt may give rise to the production of lead-regulus. The addition of fluor-spar as a flux may be desirable when the slags contain sulphate of baryta, with which it produces a readily fusible compound.

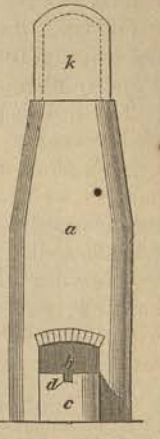


Fig. 126. Front elevation.

Description of the slag-hearth at Alport with other details.—See figs. 126, 127, 128.

a. A cylindrical hollow shaft of arch fire-bricks tapering somewhat at the upper part.

b. An arched opening.

c. The breast-pan of cast-iron, $1\frac{3}{4}''$ thick, which is U-shaped in plan; it is open at the top and bottom, and flanged where it abuts on the furnace, see fig. 128; at the top in front is a notch, *d*, through which a poker may be thrust into the interior of the furnace; at *e* is a slot, in which the tap-hole is made higher or lower as may be required; it is fixed firmly in its position and closes the lower part of the furnace in front.

b. This portion of the front opening is filled in with temporary brickwork, which it is necessary to remove from time to time without interfering with the general structure, in order to clean out and repair the interior.

f. A pot of cast-iron, called the "kettle," to receive the reduced lead as it flows out of the tap-hole at *e*.

g. A water-twyer. There are three similar twyers at the same level having their axes horizontal; one at the back, *g*, on the line A B, and the other two opposite each other in a horizontal line drawn through the centre of the furnace at right-angles to the line A B; they are $3\frac{1}{2}''$ in diameter at the small end, inside measure.

h. A sloping bed, made of a mixture of fire-clay and coke-dust. This is the *solid* bottom, and on it up to the part where the slag flows into the breast-pan, there is laid a bed of small riddled coke, which is changed once a week.

k. Arched entrance into the flue, bricked up.

o. The flue connected with the condensing arrangement to be hereafter described p. 438.

l. The feed- or charging-door, below which is a platform and a flight of steps not shown in the woodcuts.

The furnace is well braced with vertical bars of iron, encircled with strong hoops of iron. The breast-pan is filled with riddled cinders and the opening at *b* closed while the furnace is in operation. A fan-blast is used and the fuel is coke. Four men are employed, one in wheeling the slag and coke, the second in charging the furnace, the third in attending to the kettle, and the fourth in removing the black-slag. The shift lasts 12 hours, during which time about 7 tons of slag are smelted. The reduced lead filters through the cinder-bed in the breast-pan, and flows from the tap-hole into the kettle; but the cinder-bed is not hot enough to permit the slag to run through, and so it flows over the top of the breast-pan on the side opposite the tap-hole, along a sheet-iron gutter, from which it drops into water in a pit underneath. Wood is kept burning on the kettle and against that side of the breast-pan in order to prevent the lead from solidifying. The cinder-bed in the breast-pan is changed when necessary, and that is frequently. Instead of poking, as formerly, 10 or 12 times during a shift in order to keep open a passage for the lead, one end of a bar of iron, $1\frac{1}{2}''$ in diameter, is kept inserted through the tap-hole, and withdrawn occasionally to let the lead flow out, after which it is replaced.

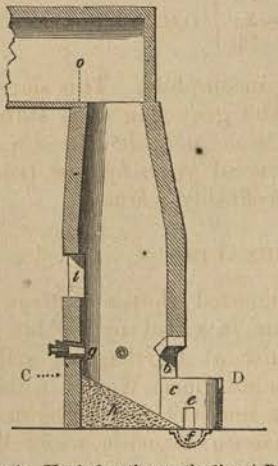


Fig. 127. Vertical section on the line A B, fig. 128.

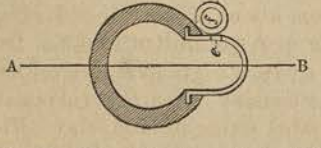
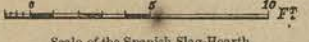


Fig. 128. Horizontal section on the line C D, fig. 127.



Scale of the Spanish Slag-Hearth.

In smelting 84 tons of slag, yielding by dry assay about 8% of lead, 10 and sometimes 12 tons of coke are consumed. Forge-cinder (chiefly tribasic silicate of protoxide of iron) and fluor-spar are occasionally required as fluxes. Some regulus collects on the top of the lead in the kettle and is taken off. The lead, when first reduced, is called "rough-lead," and must be re-melted for the market. It is slag of the kind above mentioned that is specially adapted for treatment in this furnace.

Characters and composition of the slag from the Spanish slag-hearth.—It is generally black and vitreous. One specimen, derived from the smelting of grey-slag, which I obtained from lead-smelting works at Bagillt, near Holywell, in 1859, has been analysed in my laboratory by Mr. W. Weston and found to have the following composition:—

COMPOSITION OF BLACK-SLAG.

Silica	33·94
Alumina	13·00
Lime	20·70
Protoxide of lead	10·64
Protoxide of iron	12·34
Oxide of zinc	8·78
	99·40

The composition of this slag may be nearly represented by the formula

$$Al^2O^3,SiO^3 + 3CaO,SiO^3 + \left.\begin{matrix}Fe\\Zn\\Pb\end{matrix}\right\} O,SiO^3.$$

The reduction of the lead was very incomplete. This slag-hearth was abandoned after a few trials, as the grey-slag, it is stated, was found to be too rich for it; but in the same neighbourhood a similar slag-hearth was in operation during several years for the treatment of stuff which could not otherwise be profitably worked.

CARTHAGENA FURNACES.[1]

In Spanish these furnaces are designated *Hornos de Gran Tiro*, *Hornos Economicos*, or *Pavos*.[2] They were invented by the late Juan Martin Delgado, pharmaceutical chemist at Carthagena, and first came into operation in 1847 at the Santa Lucia Works in the port of Carthagena. M. Petitgand correctly remarks that these furnaces closely resemble the native African furnaces at Kamalia, which Mungo Park described and of which an account has been given in the preceding volume on Iron and Steel. They were specially designed for smelting the poor and impure white-lead or carbonated ores of the Sierra of Carthagena, which contain from about 6% to 15% of lead and yield from 25 to 30 grammes of silver per quintal of lead, *i.e.* from 16 ozs. 8 dwts. 18 grs. to 19 ozs. 14 dwts. 12 grs. per ton of lead. These ores, according to Petitgand, "consist of earthy carbonates intimately mixed with lead [as carbonate], oxide of iron, clay, silica, and oxides of antimony and zinc; they are associated with blendic galenas (*galènes blendeuses*) and contain iron-pyrites and arsenical pyrites. These substances, occurring in infinitely variable proportions, render the smelting difficult and the reactions very complicated."[3]

[1] The following information respecting this furnace has been derived from M. Petitgand's Article in the Revue Universelle, 1861, entitled "Exploitation et Traitement des Plombs dans le midi de l'Espagne," and from MS. communications to the Author from M. Petitgand.

[2] Pavo is turkey-cock in Spanish, and Pava the hen bird. The latter term is given to the old blast-hearths, resembling our north country slag-hearth [as well as to the Castillian hearth, when a blast is used]; and they are so-called from the name of the bellows by which they are worked, Pavas. What is the resemblance between such bellows and a turkey hen?

[3] The vicinity of Carthagena was the site of vast mining operations in ancient times. According to Strabo 40,000 men were employed there, and the daily returns of silver amounted to 20,000 drachmæ.

Description of the furnace.—The annexed woodcuts (129 to 131 inclusive) have been prepared from original drawings communicated to me by M. Petitgand.

A. Chimney.
B. Foundation of solid masonry carrying the chimney.
C. Flue connecting the furnace with the chimney.
D. Charging-door (*cargador*).
E. Hearth-bottom.
F F. Peep-holes: there is one immediately above each twyer.
G G G G G G. Twyers, made of refractory clay, through which the air enters to support combustion.
H. Cinder-fall for downflow of the slag.
R. Tap-receiver, communicating with the hearth-bottom (E) by a passage, as shown by the dotted line in fig. 131.

The bottom of the furnace is made of the refractory materials of the locality mixed with finely-pounded dust of coke or charcoal, stamped down in successive layers. The draught is caused by the chimney 13 or 14 metres (say from 42′ to 46′) high. Usually one chimney serves for two furnaces, in which case it is divided by a partition wall extending upwards $\frac{2}{3}$ of the total height of the chimney. In smelting-works having condensation-chambers, the flue opens

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(*Handbook for Travellers in Spain. By Ford*, 1845, *p.* 416.) I am informed by Mr. Grote, author of the History of Greece, that the Attic drachma of the time of Polybius, from whom Strabo quoted in the foregoing passage, was equivalent to about 8¾d. English; so that 25,000 drachmæ amounted to 911*l.* 7*s.* sterling. And from a single mine, named Bœbelo, Hannibal obtained a daily return of 300 lbs. of silver. (*Pliny. Lib.* xxxiii. *c.* 31.) Ford states that on the 21st April, 1839, a lode of argentiferous galena was discovered at a depth of about 50 feet, to which the name of *La Carmen* was given in honour of the Virgin; it yielded 1800 arrobas (1 arroba = 25 lbs.) of ore per day and the shares soon rose from 150 dollars to 160,000. Petitgand remarks that "the Sierra of Carthagena is not like the Sierra of Gador bristling with precipices and escarped rocks, which render access to the latter so difficult: its metalliferous deposits are nearer the sea, and these circumstances explain why, in spite of the inferiority, often indeed poverty, of the ores, it has been so energetically worked. [A correspondent, personally acquainted with this district, informs me that another reason of their being worked so energetically is the *chance* of getting a great prize. The ores of the Sierra de Gador contain only 2 ozs. of silver per ton.] It is composed of sedimentary rocks of the ancient transition strata, argillaceous schists, slate, mica-schists forming the base of the fissured black crystalline limestones, sandstone and conglomerates. The erupted rocks are greenish and porphyritic, and they are *par excellence* the rocks accompanying nearly all the metalliferous deposits of this locality, which for the most part are in contact with schists and limestones, and extend over a large area. Although numerous veins of ore occur, yet more generally the ore exists in intercalated beds and irregular pockets in the limestones. . . . . In the district of Almazarron the erupted rocks are traversed at many points by veins of galena, which would indicate that the ore is of later date than those rocks. . . . . There are two classes of ore, carbonates and galenas, of which the former predominate. The galenas delivered to the smelters vary in produce from 15% to 60%, the average produce being from 30% to 35%, with from 45 to 170 grammes of silver per Spanish quintal of lead (46 kil. 10 grammes = 46·01 kil.): *i.e.* from 31 ozs. 19 dwts. 2 grains to 120 ozs. 14 dwts. 10 grains per ton (1 gramme = 15·438 grains). . . . . The deficiency of water throughout the entire metalliferous district of the South of Spain, added to the absence of all motive power, will ever render the dressing of the ores difficult, if not impossible."

directly into the passage leading to those chambers. Long chimneys are in more general use than such chambers. At Carthagena these furnaces are built of talcose schists set in regular courses. In other parts of the coast, as at Adra, they are built of common bricks with an internal lining of fire-bricks. The furnace is braced externally with strong bars of square wrought-iron placed vertically and encircled with strong wrought-iron hoops, as shown in fig. 129. A furnace complete costs from 2500 to 2600 francs (say from 100*l.* to 104*l.*), including the chimney, which costs not less than from 1400 to 1500 francs (say from 56*l.* to 60*l.*).

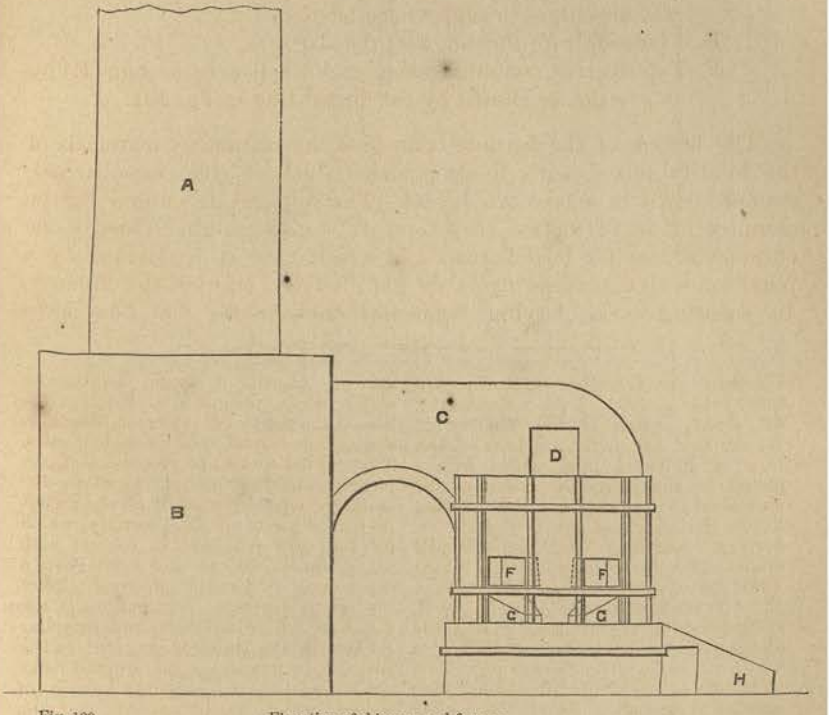

Fig. 129. Elevation of chimney and furnace.

The characteristic feature of these furnaces, it will be perceived, is that the air enters through twyers by means of a chimney-draught, and is not forced in as in blast-furnaces, by blowing-machines.

Smelting-charge.—The charge usually consists of from 50 to 60 basketfuls of ore, weighing from 6 to 7 kil. each (12·2 to 14·4 lbs.), from 10 to 12 basketfuls of slags mixed with $\frac{1}{6}$ of rich slags (*crasses*)[4] from previous smeltings, and from 6 to 7 basketfuls of coke with a little wood if necessary. The slags promote liquefaction [and as they no doubt contain lead, show the produce to be greater than it

[4] By the name *crasses blanches* Petitgand designates mixtures of so-called sub-sulphides with shots of metal disseminated, oxides, and silicates.

is in proportion to loss, which, as a correspondent quaintly remarks, may be convenient at times] and the wood tends to prevent the agglomeration of the furnace contents, which would check the draught. In the course of 24 hours from 150 to 200 Spanish quintals of ore, containing on the average from 8% to 10% or even 12% of lead, are passed through the furnace, along with from 50 to 60 Spanish quintals of slags. The proportion of old (Roman) slags is often increased, and no inconvenience arises from this, as the Carthagena furnace is well adapted to the smelting of such slags.

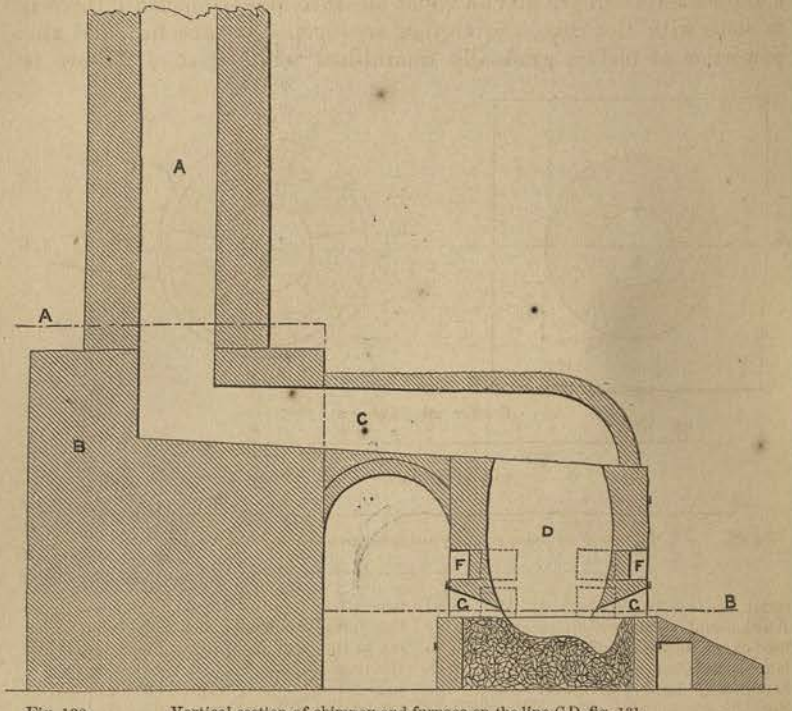

Fig. 130. Vertical section of chimney and furnace on the line C D, fig. 131.

Mode of conducting the process.—The composition of the smelting-charge of carbonated ores is extremely variable, and is regulated during the process by the master smelter according to what he observes in the working of the furnace. Petitgand praises highly these smelters for the skill with which they overcome the difficulties of the process. Coke is the fuel, but before lighting a new or repaired furnace, it is filled with wood or other convenient vegetable fuel, such as the roots of the dwarf palm (*Chamærops humilis*), the creeping stems of Atocha (*Stipa tenacissima*), etc.[5] Ignition is effected

[5] To my respected friend and former fellow-student, Mr. Giles Munby, author of the "Flore de l'Algérie," who resided many years in Algeria, and has travelled much in the south of Spain, I am indebted for the following interesting ac-

through the twyers, which in this stage are kept half closed up, and the temperature is carefully moderated so that the internal refractory clay lining may dry gradually with as little risk of cracking and flying off as possible. In about 5 or 6 hours the furnace is dry, when it is filled with coke up to the top and some hundredweights of lead are thrown in, which melt, trickle down to the bottom, and prevent the first-formed slag from sticking to the hearth and stopping up the tap-hole. As soon as the interior of the furnace has become bright red-hot, which will be the case after a few hours, 5 or 6 basketfuls of ore and an equal measure of lead-slags are thrown in along with the coke, the twyers are opened to the full, and the proportion of fuel is gradually diminished while that of the ore is

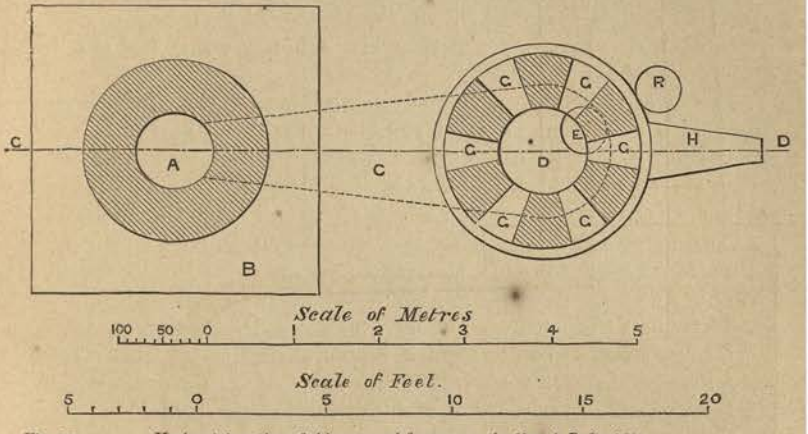

Fig. 131. Horizontal section of chimney and furnace on the line A B, fig. 130.

count of the application of the word Atocha and enumeration of the plants used as fuel in the South of Spain. "The latest published Flora of Spain by Willkomm and Lange gives *Atocha* as the Spanish name for *Stipa* (*Macrochloa*) *tenacissima*. I have always heard *Atocha* applied to the *refuse* of Esparto grass, or the dried unserviceable leaves, or even old ropes of Esparto, untwisted and used either for lighting fires, or more commonly for washing plates and dishes, for which last purpose it is rubbed between the hands so as to convert it into a substance resembling tow. The *madre d'atocha* (mother of atocha) is the dead, dried leaves of the plant, which are never pulled, as they serve to protect the living leaves. In the province of Oran (this plant does not grow near Algiers) the hills are covered with this grass; but, although Lloyd (of the *Weekly News*) has an agent at Oran for collecting it, yet all the Esparto used there for rope-making is imported from Spain, and fetches a much higher price than that of Oran. This is owing to the periodical fires which ravage the country in the province of Oran, which destroy the *madre d'atocha*, and the young leaves being tender and unprotected are eaten by cattle. The plants used as fuel in the south of Spain are as follow:—Lavandula Stoechas L.,—Rosmarinus officinalis, L.,—Cistus Clusii, Dunal,—Cistus ladaniferus, L., C. albidus, L., &c.,—Retama sphærocarpa, Webb (near Malaga),—Pistacia Lentiscus L.,—Pinus Pinsapo, Boiss (near Malaga),—Genista Scorpius, Dec., and G. linifolia L.,—Ulex provincialis, Lois,—Calycotome spinosa, Link,—Ononis Natrix, L.,—Thymus vulgaris, L.,—Teucrium fruticans, L.,—Passerina tinctoria, Wickst. (near Tortosa and Valencia),—Quercus Ilex, L., and Q. coccifera, L.,—Tamarix gallica, L.,—Rhamnus lycioides, L.. and R. Alaternus, L.,—Phillyrea media, L.,—Jasminum fruticans, L.,—Salvia officinalis, L. (Aragon).—Osyris alba, L. I have never seen wild olive-trees growing in sufficient quantities to be used as fuel."

increased. Soon afterwards somewhat pasty slag will be seen to flow out in front of the furnace. One man is constantly employed in looking after the twyers, from which he detaches with a little hook any adherent slag or other matter tending to obstruct them. When the furnace is working well the twyers are bright, and when they become dark there is derangement, owing to imperfect liquefaction of the ore with consequent agglomeration and impeded draught. This evil may arise from the descent of ore in too large lumps. If the slag runs too liquid, the proportion of galeniferous matter in the charge is increased. The charging-door is only opened at the time of charging, which should obviously be effected as quickly as possible and which takes place every hour or more frequently, according to the activity of the furnace. The charges introduced at a time are considerable, in order, as far as practicable, to lessen the disturbance caused by checking the exhausting action of the chimney when the charging-door is opened.

The relative brightness of the twyers indicates the relative temperature in the adjacent parts of the furnace within; and to this point observation should be directed. Towards the side where the temperature is seen to be highest, the ore should be thrown in larger proportion, so that the ascending gaseous current from the twyers may be more or less diverted from the circumference, where its calorific action is greatest, towards the centre in order there to accelerate fusion. And because of the higher temperature in the centre, the ore, according to Petitgand, should by preference be thrown in towards the circumference, so as to form a funnel-shaped cavity in the centre. This inconvenience, he adds, is a consequence of the construction of the furnace and of the manner of admitting the air; but it is lessened by the expedient above-mentioned and by advancing the twyers inwards as far as practicable: in this way the ascent of the gaseous current through the centre is promoted, and the temperature consequently in that part is increased, while at the same time the lining of the furnace is less acted upon. A well-managed furnace continues in operation 2 or 3 months, sometimes longer, so long as the hearth remains in a good state. It is stated that a furnace hardly gets into steady regular working before the lapse of 12 or 15 days. The twyers wear away quickly, and have frequently to be renewed. Use is made of the peep-holes above the twyers to detach the slaggy matter which is constantly accumulating above the latter, and which otherwise would soon stop them up completely. The thinness of the walls in this part of the furnace facilitates this operation.

The furnace is tapped every 6 hours [or oftener as occasion may require?], when the metal runs into the cavity on the outside. It is rabbled during some instants with a few pieces of wood, after which, as soon as it has become tranquil, it is skimmed to remove any supernatant rich slag (*crasses*), and then cast into pigs weighing from 45 to 52 kil. each (99¼ to 114½ lbs.), the proper and customary weight in all the lead-smelting works of the coast. All the lead of Carthagena is hard, whether derived from the carbonates or from

galenas smelted by themselves in other furnaces, and is usually subjected to the softening process. It contains from 70 to 75 grammes of silver per 100 kil., *i.e.* about from 22·4 to 24·0 ozs. per ton. [An experienced correspondent informs me that he considers this produce to be much too low, and that it is from 35 to 70 ozs. per ton of lead.] With the usual smelting-mixture of about 12% produce, the yield may be estimated at about 9%, so that the loss amounts to about 3%, or 25% of the total lead; and, supposing the produce to have been determined by dry assay, the loss must be considerably greater. The same correspondent doubts this statement, and believes the loss to be nearly 50%; much, however, depends upon the mode of existence of the lead in the charge, not only chemically but, what is even more important, *mechanically*.

Smelting-costs :—

200 quintals of ores[6] = 9200 kilogrammes ... } value not stated. 50 to 60 quintals of slags ... }				
Fuel 33½ to 35 quintals at 13 reals, say ...			400 reals.	
On the average, say, 1500 kil. ...				104 francs.
Labour ...	2 master smelters at ... 12 reals	24 reals		
	2 assistants at ... 6 ,,	12 ,,		
	4 labourers at ... 5 ,,	20 ,,		
	Breaking and mixing ores, &c. ...	22 ,,		
	4 lads to take away slags ...	18 ,,		
	1 overlooker ...	8 ,,	104 ,,	27·05 ,,
Wear and repair of tools ...		24 ,,		
Clay, water, twyers, wear of furnace ...		40 ,,	64 ,,	16·65 ,,
			568 ,,	147·70 ,,

In the preceding computation the Spanish is reduced to French money, at the rate of 26 centimes per real, or the mean between the extreme exchanges of 25 and 27 centimes. The special smelting-costs on 9200 kilogrammes of ore, yielding 850 kil. of lead, are therefore 5*l.* 18*s.* 2*d.*, and, consequently, 6*l.* 19*s.* 1*d.* per ton of lead of 1000 kilogrammes.

According to the experience of Mr. Thomas, the cost of smelting carbonates yielding 12% of lead in the Carthagena furnace, is 34 reals per quintal of lead produced, *i.e.* 748 reals per statute ton of lead; and the consumption of coal is 1 cwt. 1 qr. 18 lbs. per quintal, *i.e.* 1 ton 11 cwts. per ton of lead.

Remarks on the Carthagena furnace.—Although the term economical has been applied to these furnaces from their working without the aid of blowing-apparatus, whereby a daily saving of from 16 to 22 francs per furnace is effected, yet, as Petitgand observes, that term is illusory, and notwithstanding the saving just mentioned, their success would have been questionable if larger quantities of ore had not in a given time been smelted in them than in the usual blast-furnaces [my correspondent above referred to denies the accuracy of this statement].

[6] 1 quintal = 46·01 kilogrammes.

It is only in this latter respect that their adoption can be justified; and they do not become really economical until the accidents and difficulties (*embarras*), which occur during some time after they are first lighted, have been surmounted. "They have," writes Petitgand, "maintained and largely contributed to the development of the mines and metallurgy of Carthagena: it is to them that it owes its pre-eminence. For the ores of this district they fulfil conditions which are not found combined in the ancient furnaces. They have greater capacity, a larger hearth, an arrangement for giving access to atmospheric air at several points simultaneously, and therefore an excess of oxygen, which is indispensable for reduction: they facilitate the mixtures of very diverse matters which it is necessary to treat together, mostly in order to act upon the gangues and decompose them; moreover, they permit small ore to be passed through in larger quantity." But it is asserted that the volatilization of lead is greater in these furnaces than in furnaces supplied with artificial blast.

Now if, as is alleged, the chief object of these furnaces is the treatment of *carbonated* ores of lead, the reason for an excess of oxygen in the interior cannot be admitted, because the condition required for the reduction of such ores is precisely the reverse of an excess of oxygen. The same is also true with respect to the reduction of Roman slags which contain lead in an oxidized state. One point upon which, as above stated, Petitgand lays stress, deserves special attention, namely, the larger quantity of ore smelted in a given time in the Carthagena furnaces than in the blast-furnaces in use in the south of Spain. The questions then arise whether this result is due to the greater capacity of the former furnaces, or to the mode of introducing the air to support combustion, or to both? Is it that a temperature sufficient for reduction prevails through a larger extent in these furnaces, and if so, why? To these questions I have received decided negative answers from a friend of much experience, who advances one fact which is conclusive: it is, that when a Pavo is turned into a Pava by a blast, it will smelt more stuff with less fuel.

The high price of fuel in the south of Spain must, as Petitgand asserts, be a serious drawback to these furnaces, coke costing 85 francs and coal 45 francs per ton delivered at the smelting-works. From the profit of the smelter computed from the *special* smelting-costs, must be deducted *general* expenses and an *ad valorem* duty of 5%[7] on the lead, so that his nett profit must be very small, and sometimes nothing. In most cases it is only the content of silver in the lead that renders the operation profitable. Petitgand properly insists upon the impolicy of the Spanish Government levying an import duty on foreign coal with a view of protecting their native collieries which are situated in distant and, so far as concerns the south of Spain, in almost inaccessible districts.[8]

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[7] This duty has since been reduced to 3%.

[8] The only coal-fields in the south of Spain are those of Belmez and Espiel, near Cordova, and the coal from those localities cannot compete in price with English coal in the southern parts of Spain.

Petitgand has seen the Carthagena furnace employed at Lanteira in the Sierra Nevada, but without much profit, for the production of regulus from pyritic copper ores; and in Catalonia unsuccessfully for the smelting of quartzose galenas. These furnaces have also been tried without more success in the province of Guadalajara in Estremadura, and in France for the smelting of galena from Algiers and Sardinia, with and without the association of carbonates. In 1859 they were still in use at some works for the treatment of grey-slags, but in 1869, it is doubtful whether even one was in operation; they were still in use at Villaricos and Adra for the treatment of slags.

Cost of reduction of grey-slags in the Carthagena furnace.—The smelting-charge is composed of about 92·5% of these slags, yielding about 16% of lead, and 7·5% of the following matters, containing about 15% of lead, viz., argentiferous galena from Almagrera in very small proportion, carbonates, refuse of ore collected about the furnaces, fume, and slag from the softening-furnaces. As the result is the same whether the slags are reduced separately or in admixture with those matters, Petitgand gives the following tabular statement of expenditure:—

185 Spanish quintals of grey-slags			8510	kilogrammes.
15 ,, ,, of fume and various slags			690	,,
			9200	,,
Fuel (coke), 26 quintals at 13 reals per quintal	= 338 reals	=	1200	... 87·90 francs.
2 smelters at 14 reals	28 ,,			
2 assistants at 6 ,,	12 ,,			
4 labourers at 5 ,,	20 ,,			
1 overlooker	8 ,,			
Breakage and carriage of materials	28 ,,			
	96 ,,			25·00 ,,
Wear and repair of tools	20 reals.			
Bricks and maintenance of furnaces	35 ,,			
	55 ,,			14·30 ,,
				127·20 ,,
		Or	£5	6 0

The yield of lead varies from 1400 to 1600 kilogrammes, say 1500, or in round numbers about 1½ statute ton. The special costs per ton of lead amount to about 84·7 francs, *i.e.* 3*l.* 5*s.* 7*d.* The lead is hard and contains from 40 to 55 grammes of silver per 100 kil., *i.e.* from 12 ozs. 17 dwts. 17 grs. to 17 ozs. 14 dwts. 8 grs. per ton. According to the data procured by Petitgand, the treatment of the matters above stated is decidedly more economical than in the old blast-furnaces or *pavas*, the difference in favour of the former exceeding 30 francs per ton of lead produced.

Smelting of Lead Ore in which the Lead exists as Sulphate.

In 1859 I saw a large quantity of lead ore from Australia at the Smelting Works of Messrs. Newton, Keates, and Co., at Bagillt, near Holywell, Flintshire; and I was informed by Mr. John Henry, the manager, that the lead existed in it as sulphate, that several hundred tons of such ore had been imported, and that it contained 38% of lead (by assay in the iron-dish), 31½ ozs. of silver per ton of ore, with some gold.

Nature of the Ore.—It is earthy and reddish-brown; and contains fragments of mica-schist; and it has been found to be composed as follows by Smith and Ward (Analysis in my laboratory, 1870):—

Composition of Australian Lead Ore.

Sulphuric acid			20·66
Protoxide of lead			42·34
Sesquioxide of iron	(as FeO = 17·24)		16·91
Protoxide of iron			2·02
Oxide of manganese	(MnO^2)		0·10
Alumina			1·09
Lime			0·21
Silver			0·10
Copper	(as CuO = 0·34)		0·27
Zinc	(as ZnO = 0·30)		0·24
Antimony	(as SbO^4 = 0·14)		0·11
Nickel and Cobalt	(as (NiCo)O = 0·026)		0·02
Silica (soluble)			0·12
Phosphoric acid			0·02
Water, combined			3·48
Residue insoluble in hydrochloric acid	Silica	10·44	13·09
	Alumina, with a little sesquioxide of iron	1·81	
	Magnesia, alkalis, and trace of lime	0·84	
			100·78
Lead %			39·30

Silver, per ton of ore, 32 ozs. 6 cwts. 19 grains.

A very small portion of sulphur is present in the state of sulphide. The quantity of sulphuric acid required to combine with 42·34 of protoxide of lead, in order to form the neutral salt, is 15·19, so that 5·47 of the total sulphuric acid present must be in combination with other bases, probably with oxide of iron for the most part. Both the sulphate of lead and this oxide may have proceeded from atmospheric action on galena associated with iron-pyrites. The insoluble residue mainly consisted of siliceous sand, with intermixed particles of white mica.

Process of smelting.—I am indebted to Mr. Henry for the following account of the method of smelting which he adopted for this ore, and of the results obtained. It was smelted in the flowing-furnace (see p. 257) with the addition of oxide of iron and culm. A smelting-charge was composed as follows:—

Ore (1 cwt. = 120 lbs.)	25 cwts.
Culm	1½ ,,
Burnt residue of iron-pyrites from soda works.....	1 ,,
Scrap cast-iron put in behind the tap-hole	0¾ ,,

Three such charges were smelted in one furnace in 24 hours, and tapping occurred once in 8 hours. The products were lead, regulus, and slag. The lead was hard and was *directly* cupelled: it yielded 130 ozs. of silver per ton, containing some gold. The slag resembled tap-cinder (tribasic silicate of protoxide of iron of puddling-furnaces), and yielded about 2% of lead, by assay in the iron-dish. The regulus amounted to about ¾ cwt. per charge; it was broken up, roasted in intermixture with a little lime in order to prevent clotting, and smelted with the addition of a small quantity of culm (see Appendix). The products were lead, containing about 40 ozs. of silver per ton, regulus, and slag. This second regulus was broken up, roasted and smelted with the addition of lime and a small quantity of culm and iron, when a third regulus was obtained, in which the copper had become concentrated, and which, accordingly, was sold to copper-smelters.

All the gold in the ore was paid for, except 5 grains per lb. Troy of silver, which were allowed to the smelter to cover the expense of parting, *i.e.* extracting the gold from the silver.

Theory of the process.—The objects sought to be attained are as far as practicable the reduction of the sulphate of lead by carbonaceous matter, the desulphurization by metallic iron of any sulphide of lead which may be formed during such reduction, and the removal of the so-called earthy bases in the state of tribasic siliceous slag. The ore contains 10·56% of silica, and, calculating the iron as protoxide, 17·24% of that oxide; but that quantity of silica would require nearly 25 parts of protoxide of iron for combination, according to the formula $3FeO,SiO^3$. The silica present in the ore more than suffices for the formation of tribasic slag inclusive of the earthy bases, so that the addition of oxide of iron or other strong base is indicated. It is desirable that there should be a sufficiency of strong base in the smelting-mixture in order to prevent as much as possible the escape of lead in the slag in the state of silicate. With regard to the metals contained in the ore, besides iron, lead and those of the earthy bases, it is not necessary to make any observations, as they are present in too small quantities to exert any practical influence; and, moreover, their action has been fully considered in the descriptions of various lead-smelting processes given elsewhere in this volume. As to the treatment of the regulus, I confess I do not understand the principle of the process that was followed.

Experiments on the reduction of Artificial Sulphate of Lead on the large scale in furnaces.

Rivot and Phillips in 1848 attempted to reduce artificial sulphate of lead in reverberatory furnaces, and seem to have failed signally in a metallurgical as well as economical point of view. Rivot asserts

somewhat dogmatically that "in the treatment both of ores and artificial sulphates you must always begin by transforming the sulphate into silicate of lead."[1] This is to be done by fritting and afterwards fusing an intimate mixture of the sulphate with 20% of silica and 1½% of very finely pulverized wood-charcoal. The object of adding charcoal is to promote the decomposition of the sulphate of lead by the silica, just as in the analogous case in the manufacture of crown-glass carbonaceous matter is added to the mixture of sulphate of soda and silica for the purpose of facilitating the formation of silicate of soda by reducing the sulphuric acid of the sulphate to sulphurous acid. The proportion of carbon theoretically needed is that which suffices to reduce sulphuric to sulphurous acid. Rivot remarks, "in the first stage, it is not sought to obtain metallic lead, because it would be mixed with a certain proportion of subsulphide, resulting from the action of the charcoal upon the sulphate." The reason here assigned is not satisfactory; for, supposing some sulphide of lead to be separated along with the lead and form the so-called sub-sulphide, it has been shown that practically the whole of the sulphide rises to the surface of the lead during slow solidification; and, if it did not, nothing would be easier than to eliminate the sulphur of the residual sulphide by the simple operation of softening.

The silicate of lead obtained as above may be smelted in a reverberatory furnace with the addition of iron, or carbonaceous matter; but whichever of these reducing agents was selected, and however carefully the process was conducted, it was impracticable, according to Rivot, to avoid the production of slags containing from 18% to 20% of lead. Moreover, the loss due to volatilization is said to have been very large. When iron, either wrought or cast, was employed as the reducing agent, and thrown upon the molten silicate of lead, it speedily subsided to the bottom of the furnace, and even by the most persevering rabbling could not be kept sufficiently in contact with the mass for complete reduction of the oxide of lead. Moreover, the lead separated contained very fine particles of iron mechanically suspended, even when the precaution was taken to add a less proportion of iron than sufficed for complete reduction of the oxide of lead.

Another method tried was mixing the molten silicate of lead with iron-pyrites to the amount of 20% or 22% of the dried sulphate of lead, and rabbling repeatedly. At first sulphur, afterwards sulphurous acid, was disengaged, and the completion of the reactions was indicated by the tranquil state of the fused mass. Two products were obtained, lead and rich slag; but with a larger proportion of iron-pyrites than above stated, lead-regulus of varying richness and poor slag were formed. This difference in the nature of the products should be noted; and it is thus explained by Rivot. The iron-pyrites, on being quickly and strongly heated, evolves part of its sulphur, which reduces some of the oxide of lead with the formation of sul-

[1] Principes Généraux, 1860, 2. p. 224.

phurous acid (See p. 30, sulphur heated with silicate of lead); then follows the reaction between protosulphide of iron and silicate of lead, whereby sulphurous acid is set free, and lead is reduced, and silicate of protoxide of iron formed so long as the slags continue rich. Rivot adds, "the action differs only when the silicates have become poor in lead, or when there is excess of pyrites in certain parts. In this case, indeed, the iron alone oxidizes at the expense of the oxide of lead, while the sulphur combines, in part at least, with the reduced lead; a regulus is formed, which rapidly melts and falls upon the bed underneath the silicate, on which it (the pyrites) acts only very slowly."[2] It is probable that consecutive and somewhat complicated reactions occur under such conditions; and the reader is advised here to refer to the following subjects in this volume:—*Silicate of lead heated with protosulphide of iron*, p. 31,—*Sulphide of lead heated with silicate of lead*, p. 48,—*Sulphide of lead heated with tribasic silicate of protoxide of iron*, p. 58.

When the blast-furnace is used in the reduction of sulphate of lead, Rivot insists that this salt should first be converted into silicate in the manner described, the remaining part of the treatment being the same as that adopted for the ores of Commern (see p. 350 of this volume). Such a method of reducing sulphate of lead has, it is stated, been pursued in an establishment in the South of France. But opinions, resting merely on personal authority, however respectable and even weighty it may be, will not produce conviction in the absence of positive experimental proof.

Smelting of Lead Ores containing the Lead as Carbonate or Carbonate and Phosphate.

Such ores are raised in Derbyshire, and those which contain phosphate, intermixed with carbonate of lead in variable proportions, are locally designated "linnets," owing to their linnet-like colour from the presence of that phosphate. I have received seven samples of ore from the Alport Smelting Works, of which five are labelled carbonates and two phosphates, yet all are designated "linnets." Two of these samples have been examined by Smith in my laboratory, one in which the lead was correctly stated to be present as carbonate, has been found to contain 24·6% of lead (which corresponds to 31·7% of neutral carbonate) and 0·0025% of silver (= 16 dwts. 8 grs. per ton of ore, or 3 ozs. 6 dwts. 15 grains per ton of lead), with only traces of phosphoric acid and 56·6% of matter insoluble in nitro-hydrochloric acid: the other, in which the lead was stated to be present partly as phosphate, has been found to contain 35·1% of lead and 0·0068% of silver (= 2 ozs. 4 dwts. 10 grains per ton of ore, or 6 ozs. 6 dwts. 18 grains per ton of lead), and 2·62% of phosphoric acid, which corresponds to 16·7% of phosphate of lead (pyromorphite), leaving 22·4% of lead, which corresponds to 28·9% of carbonate (cerussite); this ore con-

[2] Op. cit. p. 217.

tained a few specks of galena and 41·83% of matter insoluble in nitro-hydrochloric acid.

At the Alport Smelting Works, these ores are smelted in the Spanish slag-hearth in conjunction with an intimate mixture composed of old lead-slags, hard or "round," or disintegrated, from various localities, black slags from the slag-hearth when impregnated with lead in notable quantity, lumps from the breast-pan of the same hearth, and slime-ores. The "linnets" are kept in a heap by themselves. There are, then, three heaps placed on a stage near the charging-hole from which the furnace-man has to select, namely, one of slag-mixture, a second of "linnets," and a third of coke. In charging, the slag-mixture and coke are generally thrown first into the furnace and the "linnets" are strewn on the top around the wall, so as almost completely to keep down the flame. By introducing "linnets" or small slag in this manner, it is alleged that the brick-work is prevented from becoming too strongly heated. Formerly when more large or "round" slag could be had, a larger quantity of "linnets" could be smelted in the blast-furnace than at present, when nearly all the old slag obtainable is in a slime-like state.

The theory of the process will be sufficiently understood from what has been previously advanced respecting ore and slag-smelting in blast-furnaces. Complete reduction of phosphate of lead is effected by contact with incandescent carbon, and the resulting lead is free from phosphorus. (See p. 76 of this volume.)

Wet Process for extracting Lead from Carbonated Ores.

I was informed by my friend, Dr. Wedding, March, 1868, that a wet process, known as Bischof's, had been introduced at Maubach, near Commern, for the extraction of lead from carbonated ores, and that hydrochloric acid was the agent employed. I have not received any further information concerning this process.

CONDENSATION OF LEAD-FUME.

In 1778 Bishop Watson published an essay on "Derbyshire lead ore," in which he directed attention to the fact that lead was sublimed in notable quantity during the smelting of galena, of which part adhered to the internal surface of the chimney and part escaped from the top of the chimney into the air, falling upon the ground and poisoning the water and herbage upon which it settled.[1] He suggested, that "this sublimed lead might be collected either by making it meet with water, or with the vapour of water during its ascent, or by making it pass through an horizontal chimney of a sufficient length." The suggestion was received by Derbyshire lead-smelters as "a very rational one. But," writes the Bishop, "so difficult is it to wean artists from their ancient ways of operating, that

[1] Chemical Essays, 1782, 3. p. 240 and p. 282.

I question very much whether any of them would ever have adopted the plan they approved, if an horizontal chimney which was built a little time ago in *Middleton Dale* for a quite different purpose, had not given them a full proof of the practicability of saving the sublimate of lead, which is lost in the ordinary method of smelting. This chimney was built on the side of a hill, to prevent some adjoining pastures from being injured by the smoke of the furnace. It not only answers that end, but it is found also to collect considerable quantities of the lead, which is sublimed during the smelting of the ore; this sublimed lead is of a whitish cast, and is sold to the painters at 10 or 12 pounds a ton." The injury to the pastures, it needs scarcely be remarked, must have been caused in part, and probably for the most part, by the sulphurous acid of the smoke. The smoke from lead-smelting furnaces consists of the gaseous products derived from the combustion of the fuel and the oxidation of the ore, the nitrogen of the atmospheric air which supports combustion with more or less of free oxygen, and of lead or certain compounds of lead partly sublimed and partly carried off in mechanical suspension. The term fume is technically restricted to the solid matter rich in lead that is deposited. Now, when the word condensation is applied to lead-smoke, it is generally understood to mean the condensation of the *fume* and not of the *sulphurous acid*. But as this acid is exceedingly destructive to vegetation, it is very desirable that it should be condensed and, if practicable, utilized. The condensation of the sulphurous acid in lead-smoke is one thing and the condensation of lead-fume is another. It is important to bear in mind this distinction.

This story of the introduction of the long horizontal chimney is not only interesting but teaches a lesson to smelters and manufacturers of the present day; for it shows that in one case at least, the suppression or diminution of a nuisance, caused by the escape of deleterious smoke into the air, was attended with substantial advantage to those who produced it. And there is reason for believing that if compulsory legislation were adopted or the existing law were put in force with respect to smoke of various kinds which is still permitted to blacken or contaminate the atmosphere, especially of our great manufacturing towns, the authors of the nuisance would be benefited as well as the public. So long as manufacturers are prosperous it is only natural that they should favour the let-well-alone system, regardless of the comfort and healthiness of the population affected. That system, however, ought no longer to be tolerated: and, failing voluntary action in the matter, the law, if not already sufficient, should be made strong enough to enforce what is so manifestly expedient and at the same time just. Well did Bishop Watson comment upon the difficulty of weaning smelters and others from their ancient ways; for even now there are some lead-smelting works in England, where the smoke is allowed to escape wastefully from low chimneys and exert its noxious effect upon the herbage and cattle within its reach!

The condensation and collection of lead-fume from lead-smelting furnaces or others in which lead is exposed to high temperatures, has from time to time, particularly in recent years, been the subject of much consideration, and of numerous patents. The problem is difficult of solution, and as yet no method has been discovered which is completely effectual and in every respect satisfactory. The fume being in a state of extremely fine division is, notwithstanding its comparatively high specific gravity, kept long in suspension in the air however tranquil. It is only deposited slowly, and the condition which might *à priori* seem to be most favourable for its deposition is that of least movement of the air. Accordingly, it will be found that in many of the plans devised for the purpose in question, it has been sought to approximate as far as practicable to that condition. Thus the smoke from the furnace has been made to pass through large chambers in its course to a vertical stack or chimney. Suppose, for the sake of argument, that the sectional area of the furnace-flue where it enters such a chamber to be 1 square foot,—the sectional area of the chamber 100 square feet,—and the sectional area of the outlet-flue directly connected with the stack 1 square foot. Now, it is evident that if all the air[2] within the chamber were moving at the same velocity, it would travel one hundred times less rapidly than in the inlet and outlet-flues. If the interior of the chamber were clear or vacant (*i.e.* wholly free from obstructions) the air within it would certainly not move with uniform velocity, and the course of highest velocity would be in a direct line from the inlet to the outlet-flue. This inequality of velocity may, however, be in a great degree, if not entirely, obviated by adjusting partitions in the chamber so as to cause the air in its passage through to take a very tortuous course. With such an arrangement it may be necessary to aid or supersede the exhausting power of a vertical stack by machines either of propulsion or of exhaustion, such as fans and air-pumps. In the foregoing remarks no account has been taken of the effect upon velocity due to the difference of temperature in the smoke when it enters and leaves the chamber, because the argument is not thereby sensibly affected.

Large chambers have been carefully tried, and not found to be effective in proportion to their size, though every precaution may have been taken to prevent the smoke from passing directly from the inlet to the outlet.

With a view to promote the deposition of the fume in condensation-chambers, the smoke has been exposed to the action of fine jets of water or artificial rain, or steam has been injected into the chamber, which, subsequently condensing, would tend to carry down the fume. Of all the modes of applying water in lead-fume-condensing arrangements, this of steam would, *à priori*, seem likely to give the best result; for steam, it may be conceived, would be everywhere intimately mixed with the smoke, and would on condensation

[2] By the term air is here meant the gaseous contents of the chambers, and the finely-divided matter suspended mechanically.

be much more likely to *moisten* and seize the finely-divided particles constituting fume than water introduced in the state of rain, but experience has not confirmed this anticipation. The smoke has also been forced through water by means of large exhausting pumps or otherwise.

But of all the methods which have been tried on the large scale, the old long horizontal flue has been found to be the simplest, one of the least expensive, so far as maintenance is concerned, and one of the most effective. This arrangement, however, is only practicable in certain districts, such as among the barren hills of Derbyshire or Cumberland. In every case the flue must end in a vertical stack sufficiently high to produce the necessary draught in the furnaces with which it may be connected. Owing to the comparatively large sectional area of these long flues, they act in a certain degree like condensation-chambers of much larger sectional area; but *time* is only one element in their action. Although the fume may remain suspended in the air for a long while, yet it is always in process of deposition. In a flue of great length, say a mile or more, a notable period elapses between the entrance of the smoke and its arrival at the distant stack; and during the whole of this period fume is being deposited. Besides, there is retardation of the current by friction against the walls of the flue which must sensibly favour the settling down of the fume; and there appears to be also an adhesive action exerted by surfaces, to which the fume sticks and falls down at intervals in the form of flakes. These flues are arched over, and must have openings at intervals through which men may enter and bring out the fume. While the furnaces are in operation such openings, it needs hardly be stated, must be bricked up or otherwise tightly closed. The flues should where practicable have a gentle inclination upwards towards the terminal stack; or they may as in some localities be built in zig-zag on the side of a hill. Care should be taken in scrambling or walking over them. Some years ago my friend, Dr. Day, professor at the University of St. Andrews, in the course of a country ramble fell into one, broke his arm, and was nearly suffocated by the sulphurous acid.

The general principles involved in lead-fume-condensing arrangements having been expounded, particular instances will be considered under the following heads:

1. Long horizontal flues.
2. Condensation-chambers.
3. Exposure to artificial rain.
4. Forcing through water.
5. Intermixture with steam and its subsequent condensation.

I have selected for particular description and illustration various arrangements for the condensation of lead-fume which may be regarded as more or less typical; and in some of these one or more, or even all the principles above enumerated, are applied in combination.

Several of the patents granted in this country for alleged improvements in the condensation of the fume differ from each other only in small and comparatively unimportant details; and it is certain that if supervision, properly so called, had been exercised by the legal authorities charged with the granting of patents, several of the patents in question would never have been obtained.

Long Horizontal Flues.

For the following statements as to the length of these flues at the smelting-works of Mr. Beaumont, in the north of England, I am indebted to Mr. Sopwith, who communicated them to me in January 1865.

Two flues at Allen Smelt Mill	one	4451	yards long.
	the other	4338	,,
Flue at Allenheads Mill		3424	,,
Flue at Rookhope Mill		2548	,,
		14,761	,,

The total length of the above flues is 8 miles 3 furlongs 21 yards. The transverse area of these flues varies a little, but usually they are 8′ high and 6′ wide. Mr. Sopwith informed me, that in one year 800 tons of lead were extracted from the fume taken out of these flues; but it is doubtful whether that quantity was deposited in a single year.

Foster, in 1821, describes these flues as carried nearly in a horizontal position for more than 100 yards, and terminating in a vertical stack; and he states that generally they were 5′ high and 3′ broad, inside measure. The profit arising from them generally repaid the cost of their erection, while the neighbouring land and the cattle grazing upon it were thereby in a considerable degree freed from the pernicious effect of the lead-fume.[3]

Condensing arrangement at the Alport Lead-smelting Works, Derbyshire.

This arrangement is shown in the annexed woodcuts, which have been prepared from drawings kindly obtained for me by Mr. Francis Barker, of Bakewell. The smelting-works are situated in a valley at the foot of a very steep hill, and it is owing to the nature of the locality that this particular system of condensation has been adopted. From the furnaces to the base of the stack the vertical height is 70′, and the stack is 34′ high.

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[3] Section of the strata, antea cit. 396.

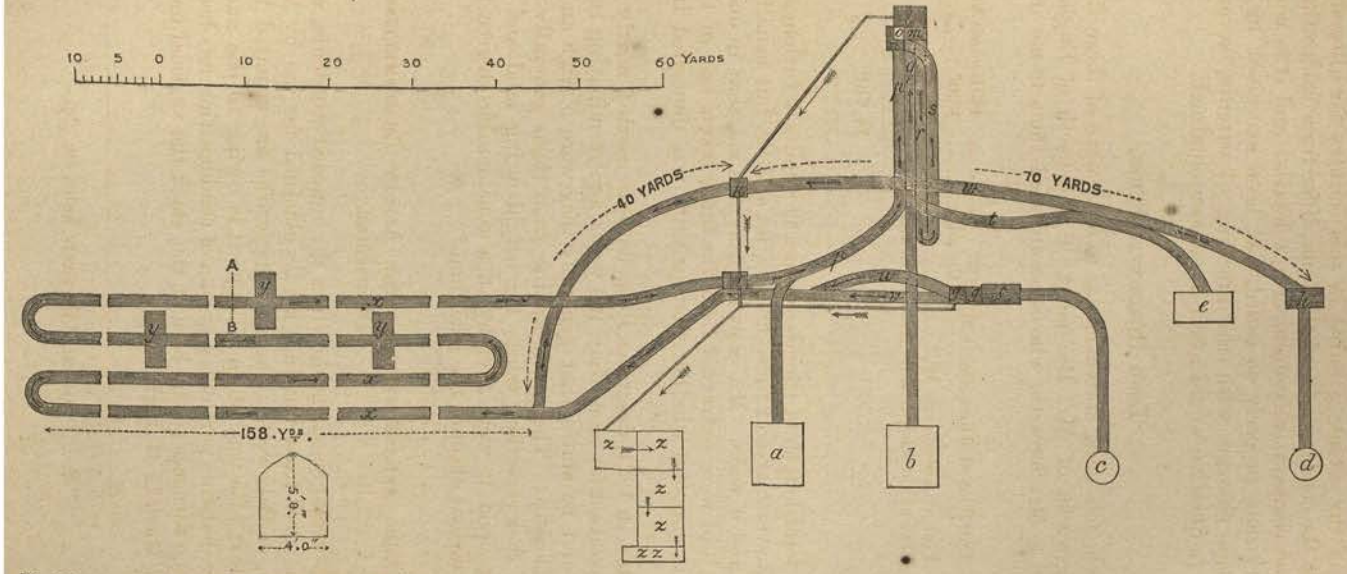

Fig. 132. Section of chimney on the line A B.

The scale applies only to the length of the flues, and not to their other dimensions, or to the dimensions of the furnaces and condensers.

a. Reverberatory furnace, in which only ore is smelted.
b. Reverberatory furnace, in which sometimes ore and sometimes fume is smelted.
c. Blast-furnace (Spanish slag-hearth).
d. Blast-furnace.
e. Calciner, not in use (December, 1868).
f. Condenser, *i.e.* chamber, 14′ long, 7′ wide, and 12′ high, into which jets of water are introduced.
g. Condenser, 12′ long and 6′ wide, which is divided into two compartments by a partition wall with holes in it, each compartment being 6′ square; the top is covered with perforated lead, through which a shower of water falls upon a layer of loose stones, and is thereby broken and dispersed.
h. Condenser, 14′ long, 7′ wide, and 11′ high, into which jets of steam are introduced.
i. Condenser, which is placed at the upper end of a long flue (*x*), and divided into two compartments; the first compartment has an area of 17′ square; at the top is a bed of heath, about 20″ thick, having an area of 36′ square; and about 4′ above is a perforated wooden roof, through which an intermittent shower of water falls upon that bed; below the heath there is a clear depth of more than 5′.
k. Condenser, of which the area is 6′ square; about half way down it contains a bed of loose stones, 1½′ thick; the roof is perforated, and a shower of water descends from it.
l. Condenser, 12′ long and 7′ wide; it contains a bed of loose stones, 1½′ thick at ⅓ the height of the chamber from the bottom.
m. Chamber.
n. Condenser, about 8′ long, 6′ wide, and 10′ high, supplied with a jet of water.
o. Vent of vertical chimney, supplied with a jet of water.
p. Flue, which receives the smoke from the long flue (*x*) and from the reverberatory furnace (*a*).
q. Flue, which conveys the smoke from the reverberatory furnace (*b*) into the chamber (*m*).
r. Flue, from the bottom of the condenser (*l*), which descends the hill and communicates with the condenser (*n*) through a flue (*s*).
s. Flue, which completes the course from (*b* and *l*) to (*n*).
t. Flue from calciner (*e*) to flue (*p*).
u. Flue from upper part of condenser (*g*), leading to long flue (*x*).
v. Flue from lower part of condenser (*g*), and joining (*u*) on the way to (*x*).
w. Flue from condenser (*h*), leading to condenser (*k*).
x. Long flue, of which the straight parts are nearly horizontal.
y. Arched chambers in the course of the long flue (*x*), each 20′ long, 7′ wide, and 7½′ high to the centre of the arch.
z. Pits, into which the water, not converted into steam in the condensers supplied with jets of water (not jets of steam), is conducted, in order that the fume suspended in it may deposit itself.
zz. The lowest water-pit, filled with cinders, on which a little fume is deposited.

The smoke from the reverberatory furnace (*a*) goes directly into the condenser (*n*) through the flue (*p*), in which it mixes with the smoke from the long flue (*x*), as indicated by the direction of the arrows. When ore is smelted in the reverberatory furnace (*b*), the smoke from it passes directly to the condenser (*n*); but when fume is smelted, the smoke is conveyed through the flue (*q*) under the shower in the condenser (*l*), passing from the bottom into the flue (*r*), down the hill towards the condenser (*g*), and returning through the flue (*s*) into the condenser (*n*). From the blast-furnace (*c*) the smoke passes into the condenser (*f*), and thence into the condenser (*g*); and from the blast-furnace (*d*) the smoke passes into the condenser (*h*), and thence through the condenser (*k*) into the long flue (*x*). Part of the smoke from the blast-furnace (*c*) enters the condenser (*g*) above the layer of loose stones and part below it; from the upper part of this condenser it passes through the flue (*u*), and from the lower part through the flue (*v*); these flues unite and, descending the hill, enter the long flue (*x*). The smoke from the calciner (*e*) passes into the condenser (*n*) through the flues (*t*) and (*p*). The return smoke from the long flue (*x*) enters the first compartment of the condenser (*i*), passes through the bed of heath in the second compartment, and thence through the flue (*p*) into the condenser (*n*). The smoke which enters the chamber (*m*) from the flue (*q*) ascends and passes from the upper part into the condenser (*l*). All the

smoke traverses the condenser (*n*) before reaching the stack (*o*). The water from the condenser (*l*) is conveyed, as indicated by arrows, into the condensers (*k* and *i*), in the latter of which it is met by a fresh jet of water.

Stagg's Condenser.

This arrangement was patented by Mr. Joseph Dickenson Stagg in 1843.[4] The essential principle is the drawing of the smoke from the furnaces through water. With this object it is made to pass in a tortuous course through a closed rectangular chamber, divided into a series of compartments by vertical, parallel, and equi-distant partitions, which only alternately reach the top and descend nearly to the bottom. The lower part of the chamber is filled with water, of which the height should be such that the smoke is compelled to pass under a partition through a certain column of water. Powerful exhaustion is effected by pumps. I saw this system in operation not long after the granting of the patent at the London Lead Company's Works, at Nent Head, Alston Moor, Cumberland. There were three large pumps working in alternation and moved by a water-wheel. The system has also been long in operation at the Dee Bank Lead Works near Holywell, where I have also seen it several times in action. There are three pumps here all moved by an 80-horse steam-engine. Some only of the smelting-furnaces, now exclusively reverberatory, and the cupellation-furnaces, are connected with the system. Great difficulty has been experienced both in the condensing-chambers and the pumps from the corrosive action of the sulphurous acid upon the materials used in the construction; but they have at length in a considerable degree been surmounted. As I have stood by the side of a Flintshire reverberatory furnace subjected to its action, I have noticed distinct pulsation in the draught, owing to the oscillation of the water in the chamber. This oscillation may in a certain degree be obviated by keeping the chamber containing the water full of "brushing" (*i.e.* faggots or brushwood) *up* to the level of the water; it acts as a drag, and prevents the water from getting into movement. The experience of Stagg's condenser, which has been gained at these works during many years, is such as to render it at least doubtful whether, in the event of the erection of new smelting-works, it would be expedient again to incur the same outlay for another of these condensers as has been there incurred. It has been observed that the water, which runs out from the condenser, is more charged with fume during the first melting-down of the calcined ore in the Flintshire furnace than at any other time; from which it may be inferred, that during that period the greatest volatilization of lead takes place.

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[4] A.D. Nov. 2. No. 9920. 'A new and improved plan for collecting, condensing, and purifying the fumes of lead, copper, and other ores and metals, &c.' Abridgments of Specifications relating to Metals and Alloys, p. 120.

Condensing arrangement at the Keld Head Mining Company's Lead-smelting Works, Wensleydale, Yorkshire.

I am indebted to Mr. W. Weston for sketches and details of this system of condensation.

The apparatus employed for the condensation of lead-fume at these works, which is known as Stokoe's, consists of two equal and similar rectangular chambers, each of which is divided into eighteen compartments. Each of these systems of chambers will be termed a condenser. The bottom of each condenser is covered with water,

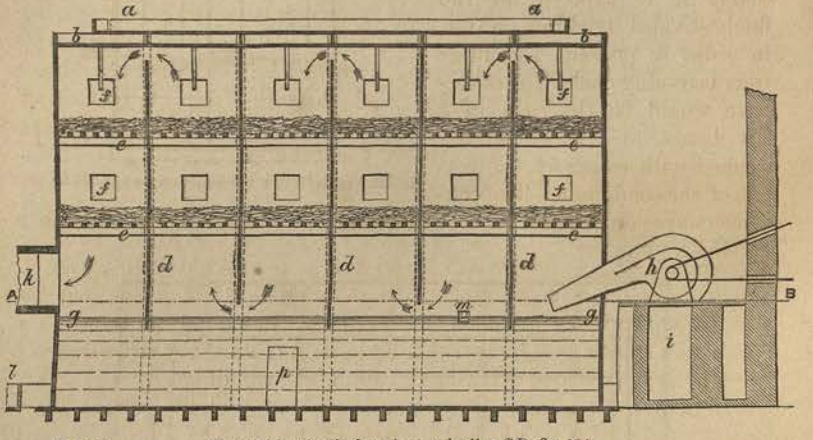

Fig. 133. Vertical longitudinal section on the line C D, fig. 134.

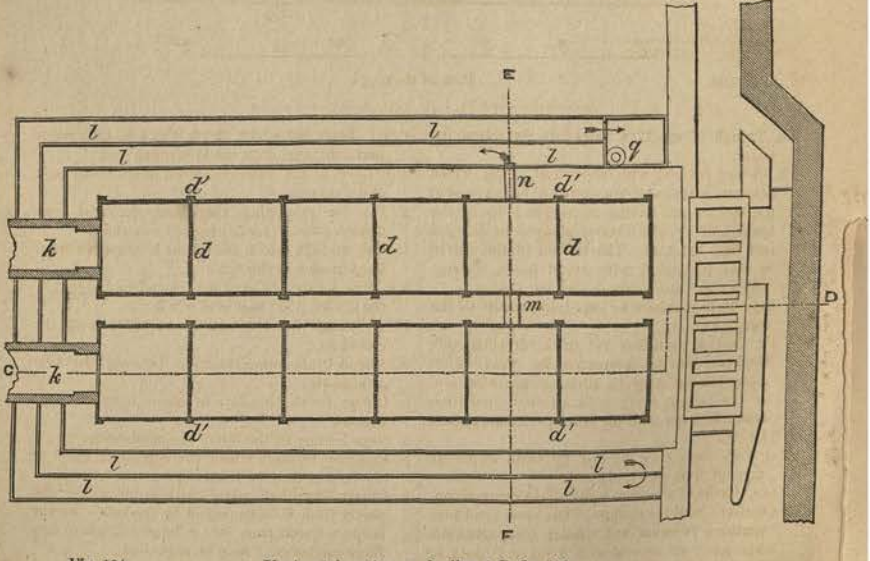

Fig. 134. Horizontal section on the line A B, fig. 133.

and from the top of each jets of water are continually falling. The floors of the two upper series of compartments are formed of joists set a certain distance apart from each other and covered with faggots. The smoke is injected by means of a fan and is compelled to pass through all the compartments of a condenser in succession; in its course it is exposed to the finely-divided trickling water, in order to prevent the filter from becoming choked, as otherwise would be the case in a few hours, and it is further washed with water at the bottom of the condenser. The condensers are constructed of 3″ battens, except the partitions which are 1½″ thick.

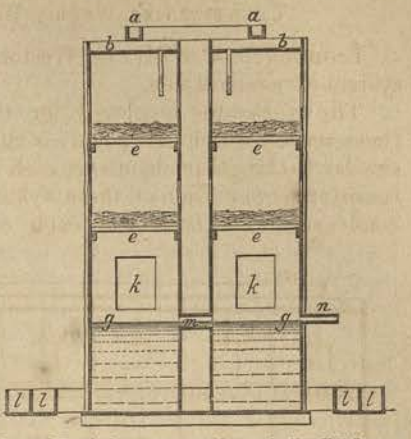

Fig. 135. Vertical transverse section on the line E F, fig. 134.

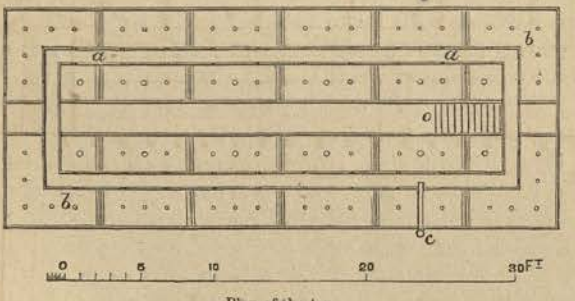

Fig. 136. Plan of the top.

a a. Trough of wood or water-box for supplying water.

b b. Cistern covered with sheet-lead, from which descends a series of zinc pipes 3′ long closed at the bottom and having numerous holes in the lower half by which water escapes in fine jets (see figs. 133, 135). The bottom of the cistern is also perforated with small holes, through which water also descends (see fig. 136).

c. Pipe 3″ in diameter for supplying water to the trough *a a*.

d d d. Vertical partitions 1½″ thick, dividing each condenser into six compartments. Space is left along the top of every alternate partition, and at the bottom every such alternate partition descends lower than the other partitions respectively.

d′ d′ d′ d′. Stays 6″ × 3″, tied by bolts which go through from side to side.

e e e e. Floors of 3″ square joists, dividing each condenser into three stories. Thus each condenser contains 18 equal and similar compartments. The joists are covered with a layer 1′ thick of faggots, or thorns, as they are termed.

f f f f. Doors, of which there is one to each compartment, except in the lowermost story.

g g. Level of the water contained in the lower part of the condenser.

h. Fan for propelling the smoke into the condensers; there is a fan to each condenser.

i. Flue through which the smoke is conveyed from the furnaces to the fan.

k k. Flue for the outlet of the uncondensable part of the smoke, 3′ 6″ high and 3′ wide.

l l l l. Trough for the outflow of water from the condenser.

m. Channel of communication between the two condensers.

n. Gutter for the outflow of water from the condensers.

o. Steps leading to the top of the condensers.

p. Doorway through which the deposit of fume at the bottom may be removed when necessary.

q. Cistern supplied partly with fresh water and partly from that conveyed by the gutter *n*; the surplus water runs into a large pit where any fume carried over may be deposited.

Condensing arrangement at the Duke of Buccleuch's Lead-smelting Works, at Wanlock Head, Dumfriesshire.

A model of this method was shown in the International Exhibition, 1851, and afterwards deposited in the Museum of the Royal School of Mines; but as the internal and essential part of the construction is concealed, it is of little value to a spectator. I have compiled the following account of it from a description, with unsatisfactory woodcut illustrations, in the Official Descriptive and Illustrated Catalogue (vol. i. p. 175). The dimensions are mainly computed from the scale attached to the woodcuts, and they should only be regarded as approximate.

This condenser is an oblong chamber in masonry, about 30′ high, 28′ long, and 6′ wide, which is divided transversely by a vertical wall about 24′ high, into two compartments, about 17′ and 8′ long respectively in the clear, which we will designate A and B. A communicates at the bottom with the furnace-flues, and B is connected at the bottom with an adjoining vertical chimney. A contains four horizontal racks about 13′ long, extending from side to side, and touching alternately the end walls, so that smoke ascending from the bottom would be compelled to take a zig-zag course. These racks are covered with large pebbles, and in the opening between the top of the partition-wall and the roof is placed a layer of coke, supported by grating of wood-work. On the top of A is a tank with a perforated bottom, from which a shower of water is kept constantly descending. There is also a tank on the top of B, of which the bottom is of iron, having twelve openings or slots about 1″ wide, extending from side to side, and placed at equal intervals from each other. On this bottom is an iron plate similarly slotted, which is made to move backwards and forwards, so that at one time the openings of this plate and of the bottom correspond, and at another do not. By this means water falls intermittently into the chamber B. A water-wheel is employed to communicate by means of a connecting-rod and crank the necessary horizontal reciprocating movement to the plate overlying the bottom. It need hardly be stated that these tanks are kept plentifully supplied with water. The water, which has fallen upon the floor of the condenser, is conveyed into reservoirs, and there left to deposit the fume which it has washed down. The beneficial results of the condenser are stated to be very manifest. Formerly the smoke from the furnaces poisoned the neighbourhood, vegetation was destroyed, and no animal could graze or bird feed near the spot; whereas now, the heather is seen in luxuriance close around the establishment, the sheep graze within a stone's throw from the base of the chimney, and game on all sides take shelter.

Fallize's Scheme of Condensing Lead-Fume.

M. Armand Fallize, a Belgian civil engineer, has suggested a plan for the condensation of lead-fume, which he considers more simple

than any employed in England, and far more perfect than those generally adopted on the continent.[5] The essential principle of his plan consists in mixing steam with the smoke after its escape from the furnaces, and subsequently exposing the mixture of smoke and steam to artificial rain, whereby the steam, it is alleged, is condensed and falls along with the water used for its condensation into a pit underneath. In this way the finely-divided solid matter, which is removed from the furnaces in the state of mechanical suspension in the smoke, would, it is supposed, be carried down and collected. The condenser proposed by Fallize may be briefly described as follows: It is a long rectangular chamber, divided longitudinally by a vertical partition extending from one end to within a certain distance of the other. Two chambers are thus formed which freely communicate at one end of the condenser. The partition is so placed that one chamber is about half the width of the other. In the middle of the wider chamber, at a certain distance apart from each other, are two vertical transverse brick walls with spaces left in every course alternating with the bricks of that course. The space included within these walls is filled with hollow perforated balls of sandstone, exactly similar to those used in soda-works for the condensation of hydrochloric acid; and the top is covered with a perforated plate of metal through which water trickles down from a cistern immediately above, and of which that plate forms the bottom. This walled space may be called the filter. The smoke is propelled into the narrower chamber (say at the left end), by means of two steam-jets, one above the other, and passes into the wider chamber where the partition falls short at the right end, which internally is rounded off in order to facilitate its progress, as here its direction is suddenly reversed. From this end or elbow it travels backwards through the wider chamber and passes through the filter in the middle, thence to the left end, contiguous to where it entered, from which it escapes, its expulsion being promoted by a steam-jet. The bottom of the condenser slopes downwards from one side to the other, and is kept constantly covered with water up to a given height; and on the outside of the condenser it communicates freely through numerous arched openings with a pit or trough extending the whole length of the condenser on the deepest side of the bottom. The bottom of the condenser is continuous with that of the trough. By this arrangement the deposited fume is expected to accumulate in that trough, and any portion still remaining suspended flows along with a stream of water running from this trough into a labyrinth, in which further deposition may occur. Along the other wall of the condenser are openings at the bottom, provided with doors, through which any deposited fume not gliding into the trough may be pushed down.

The condenser should be placed so near the furnaces that the

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[5] Revue Universelle, 1862, II. 367. The description of the scheme by M. Fallize follows his account of the condensing arrangement at the Keld Head Mining Company's Works.

temperature of the smoke may not be so low as to cause condensation of the intermixed steam. Fallize recommends as suitable for use in the erection of such a condenser bricks made of equal parts of clay and coke-dust. Should obstruction occur in the filter, the flow of water through it is to be temporarily increased, or water may be projected from a fire-engine against the outer sides of the perforated walls. We are not informed how this latter expedient can be carried into effect while smoke is passing into the condenser.

The advantages which Fallize anticipates from his condenser are these: cheapness, as a condenser adapted for smelting-works of ordinary size would cost only 5000 francs, or about 200*l.*,—the cost of generating steam would be almost nothing,—the cost of manual labour would be insignificant, as all that would be required is to remove the deposited fume from time to time,—the fume collected would be very pure, because the water of the chambers would free it from acids and soluble salts [what acids and what salts?]—in fine, the only special charge of importance would be pumping in order to maintain the water within the condenser at a constant level, and for that purpose a steam-engine of 2 or 3-horse power would suffice.

The professedly original part of the plan of Fallize is that of intermixing steam with the smoke; but it is far from novel. Bishop Watson in the last century, as already intimated, suggested the use of steam for the same purpose; and the use of steam in identically the same manner was described in two patents granted respectively to Thomas Richardson, August 21, 1848, and to Messrs. Young,[6] August 28, 1848. The same application of steam was again patented in 1859 by Mr. Alfred Courage.[7] The shower-of-rain principle has been long in operation at various lead-works, and is actually disclaimed on the ground of non-novelty in a patent granted to J. Neville in 1823.[8] I saw it employed in 1841 at lead-works then existing near Birmingham, where litharge was produced on a large scale by cupellation for conversion into white-lead, and there were some reverberatory furnaces for smelting galena.

How far the condensing-apparatus of Fallize resembles in principle that previously patented by Richardson in 1848, the reader will be able to judge from the following brief description by the latter of his process: "Injection of steam into flue between furnace and chimney, the fumes to pass afterwards into a chamber where they meet a shower of water, further divided by falling on broken bricks, coke, &c., the process being assisted (if necessary) by a steam-jet, as described by Henry Watson," in his patent for the condensation of lead-fumes, dated 1846.[9]

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[6] Smelting and Refining Lead Ore. Granted to William Young and Henry Burgess Young. A.D. 1848. Aug. 28. No. 12,256. In the specification the uncondensable part of the smoke is to be carried from the condenser under the grate-bars of the furnaces, a proposal so obviously absurd as not to require a word of comment.

[7] A.D. 1859. No. 959. 'Abridgments of the Specifications relating to Metals and Alloys,' p. 430.

[8] A.D. 1823. No. 4746.

[9] Watt's Dict. of Chemistry, 1865. 3. p. 531.

The conclusion with regard to Fallize's alleged improvements in condensing lead-smoke is that it is not original, and that steam applied in the manner described will not effect the object required. When steam in admixture with air is condensed, *mist* is the result; and this mist cannot be collected by rain either in a chamber or in the open, as may be remarked on any rainy and misty day.

Condensing arrangement at the London Lead Company's Works, called the Eggleston Mill, near Alston, Cumberland.

The drawings for the woodcuts (figs. 137, 138, 139) illustrating this condensing arrangement were prepared by one of my most promising and energetic students of the Royal School of Mines, the late Mr. Richard Thornton, who accompanied Dr. Livingstone in his last exploring expedition to Africa, and unhappily died there. Some alterations in details have, I believe, since been made; but none in the principle

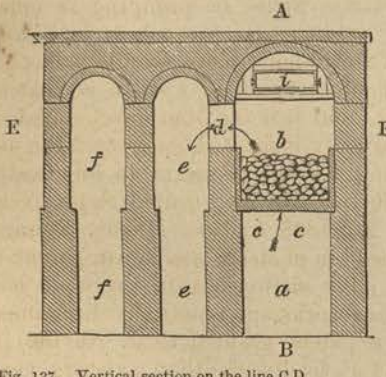

Fig. 137. Vertical section on the line C D, fig. 139.

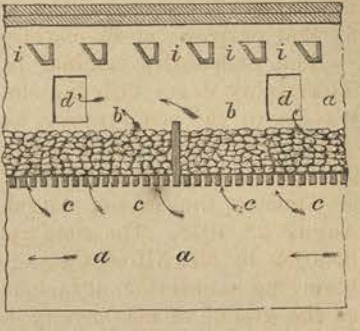

Fig. 138. Vertical section on the line A B, fig. 137, looking towards the left.

of condensation. The dotted lines in fig. 139 represent parts not in existence when the drawings were made, and which it was proposed to add, if desirable, at a future period. The smoke from the furnaces passes into the lower part of an arched flue (*a*), and upwards through a layer of large pebbles, termed "cobbles" (*b b*), resting on a bed formed of long rectangular pieces of stone set at a proper distance from each other (*c c c c*). The smoke, which escapes from the layer of pebbles into the upper part of the flue (*a a*), passes through openings (*d d*) into an adjoining flue (*e e*) and backwards for a considerable distance, when it enters the flue (*f f*), from which it proceeds forwards to the vertical chimney or stack (*g*), 21′ 9″ in diameter at the bottom, and 9′ 5″ at the top, outside measure, and 120′ in height. In the upper part of the flue (*a a*) is a series of troughs or buckets (*i i i*), suspended on trunnions at their ends. These buckets are filled with water, and tilt over intermittently, being self-acting and receiving a constant supply of fresh water. The plan of this con-

densing arrangement is not so complete as I could wish, but I hope it will be found sufficient to render the principle of construction perfectly intelligible. I am informed that of its kind it is one of the most efficient condensers in operation.

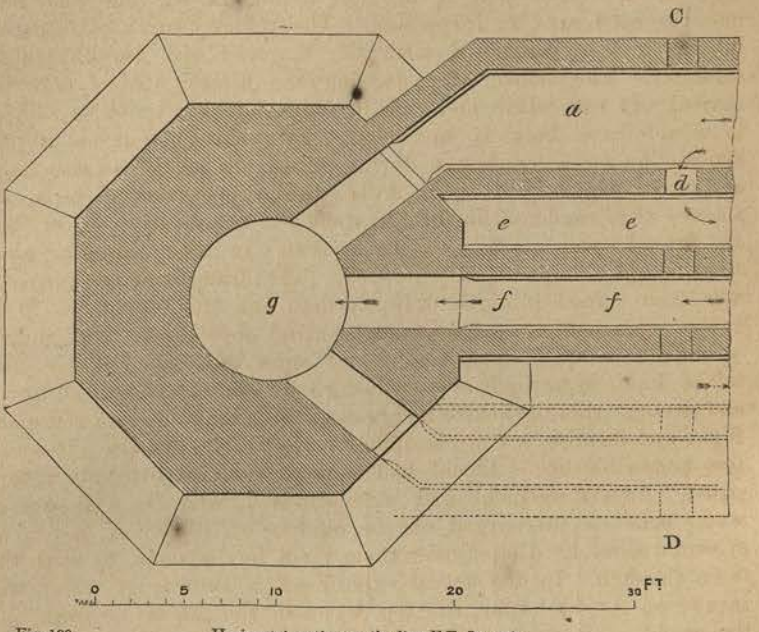

Fig. 139. Horizontal section on the line E F, fig. 137.

Observations on the Condensation of Lead-smoke by a British Smelter.

An experienced British lead-smelter, with whom I am acquainted, has made numerous trials on the large scale concerning the condensation of fume, and has communicated to me the results with the conclusions at which he arrived; and I now present them in his own words:

The following experiment was made to ascertain how far the principle of filtration could be used to remove lead-fume from air containing it. I constructed a chamber like Stokoe's (Keld Head condensing arrangement), differing in many little points for particular reasons, but not involving any change of principle. There was water at the bottom to cool the smoke, but this water was not allowed to get hot enough to produce steam. The smoke, after having been forced down close upon the surface of the water, in order to prevent it setting fire to the cinders, was made to travel up and down partitions filled with small coke (cinders from the furnaces) each piece about 1″ in diameter, and therefore very closely packed. There were

four such partitions, each about 2′ long, 2′ wide, and 6′ deep. The smoke was exhausted from two refinery-furnaces by a 4′-fan, running at full speed, which forced the smoke through the partitions and thence to the chimney; unless checked by a damper which, being closed at intervals, sent it through a hole in the flue and thus into the open air for inspection. The refinery-furnaces being at full work were connected with the fan and the draught found sufficient. The smoke after passing the filters was at once inspected. It was white and rich in fume, but not quite so rich as it would have been if unfiltered. Everything went on to my satisfaction for a few hours, during which the smoke became more and more completely purified. At length the appearance of the smoke showed that condensation or filtration was practically perfect, but the draught was not so good as at first. In about another hour the draught was practically stopped. The draught of the furnaces was then turned into the ordinary flues and the top of the filter raised. The contents presented a beautiful appearance. No cinders were to be seen: it seemed as though snow had fallen lightly, but to the depth of an inch or two inside. It was of course lead-fume, and through this the smoke had been passing, leaving more and more fume, and forming a more and more perfect filter, but also a less and less permeable one. This I had from previous experiments anticipated. An arrangement had been provided, whereby a shower of water could be discharged on the cinders, or, if I chose, a torrent of water could be dashed over them for a few seconds, to wash the fume through. In the actual experiment a shower of water was turned on for some time, the top re-closed, the fan set to work, and the smoke, after passing the wet filter, examined. The smoke contained lead-fume in quantity. The shower was stopped. After a while the filter began to choke, filtration became more and more perfect, and the draught stopped in proportion, and so on. Dashing water over the filter every half hour was tried with the same result. When the spaces between the cinders were open, the fume escaped, and when nearly stopped, it was caught, but the furnaces could not be worked. A continuous shower of water kept open certain passages through which the smoke whistled, and condensation was very ineffectual. In all cases I noticed that dry cinders sooner formed a more perfect filter than wet ones, being I suppose more porous, and the fume attaching itself by preference to a dry surface. I found no means of keeping the filter sufficiently open for a good draught, and yet sufficiently choked for good condensation of fume. Considerable draught is required both in smelting and refining lead, and any check risks the health of the workman by making him breathe an impure atmosphere.

These experiments prove to my mind that lead-smoke in air is, like a precipitate in water, capable of filtration. And I am convinced from many other experiments that, except for the difficulties arising from the heat and sulphurous acid, it would be possible to construct some textile fabric through which the smoke might be slowly forced

or drawn, leaving the bulk of the fume on one side. It appears to me that agitation or friction up to a certain point aids the fume in separating from air, as stirring a liquid assists the settlement from it of a precipitate. Wherever lead-smoke rubs on the sides of flues, there fume is most copiously deposited.

This naturally leads to the consideration of what has been often tried and still more often proposed—large chambers as a means of condensing lead-smoke. It has been thought fume would more readily settle from air at rest or nearly so in a large chamber. Such chambers, so far as I know, have failed to answer the expectation of their designers. The system was formerly tried by the firm of Mather and Co., but did not answer. I had myself occasion to build such a chamber or capacious flue for another purpose, and I observed that it did not catch much, if any, more fume than an ordinary flue of one-sixth the size: yet the uniform deposition of the fume shewed that the draught did not pass straight from the inlet to the outlet, which, indeed, was provided for in the construction of the chamber. It moved slowly along it.

Now with regard to the effect of steam and water. It is a fact that many flues pass, just after leaving the furnace, through wet ground (sandy soil below the natural drainage level) and have always 2″ or 3″ of water in them (stagnant water which does not flow along them). In these parts of the flues, according to my experience, scarcely any fume is deposited, and many of them have not been cleaned out for years. Had they been dry, they would have been full of fume long ago. I cannot explain this, but I regard it as a fact that fume deposits more freely in a dry than in a wet flue.

A favourite idea has been to saturate the smoke with steam and condense the steam in hopes of finding all the fume in the condensed water. No one who has not tried can imagine how difficult it is to condense moisture from a large bulk of hot air. It is easy enough with artificial rain, wet cokes, bricks, &c., to condense the steam to mist; but to get that mist to settle into water is the real difficulty. I have thought of leaden chambers, but the mere look of what is required in a vitriol work to overcome the heat of an insignificant fire shows how hopeless it would be to contend with the heat of a large number of furnaces in such a way.

Nothing better has I think yet been proposed than a long flue; but to construct one requires cheap land and building material, as well as a favourable configuration of country. Such a flue answers well at first, but after a few years in wet places, and after many years in all places, serious difficulties arise. The flue begins to fall, owing to the effect of the steam (moisture from the ground, &c.) and sulphurous acid on the foundations. Every stoppage disorganizes the whole work, and with a large fall it will require weeks to rebuild the flue. This may happen at a time when the smelter has engaged to deliver a quantity of lead within a given period, or under otherwise inconvenient circumstances.

The cleaning of such flues by workmen is always costly, and the

flushing of them out with water soon destroys the foundations, and the water finds its way from them to pasture lands and drinking places, unless special precautions are taken in the draining of the land. Long flues have good and bad points, but are, I think, the best condensers yet proposed. Nevertheless, those who have had most experience of them, are also those who would most willingly see some other system of condensation introduced if an equal result could be attained at less cost, in less compass, and with less inconvenience attending repairs.

Characters and Composition of Lead-Fume.

It is deposited in the state of fine powder or dust, varying in colour from grey to white. The whiteness of the smoke escaping from the chimneys connected with lead-smelting furnaces—and which every one who has had the opportunity of seeing lead-smelting works, even at a distance, must have observed—is due to the suspension of extremely fine particles of matter rich in lead. It is this matter which is slowly deposited in the track of the smoke, as it travels along, and which as before stated is then designated lead-fume or smelter's-fume. The temperature of the flues near the furnaces may be sufficient to cause the fume to agglomerate and attack the brickwork, in which case more or less vitrified masses rich in lead may be produced.

In 1859, my friend, Mr. John Henry, supplied me with three specimens of fume from the lead-smelting works at Bagillt, of which at that time he was manager. At those works there was a single lofty stack into which the smoke from the reverberatory furnaces, Flintshire and Flowing, and Spanish slag-hearth was conducted through long flues or culverts, and from these two of the specimens were collected, while the third was taken from the bottom of the stack. The three specimens have been analysed in my laboratory by Mr. W. Weston.

Composition of Lead-Fume.

	I.	II.	III.
Protoxide of lead	46·54	62·26	46·88
Sulphide of lead	4·87	1·05	—
Sesquioxide of iron and alumina	4·16	3·00	10·00
Oxide of zinc	1·60	1·60	4·14
Lime	6·07	3·77	6·73
Sulphuric acid	26·51	25·78	14·15
Insoluble residue	10·12	1·97	14·40
Carbonaceous matter	—	—	3·37
	99·87	99·43	99·67

The insoluble residue consisted chiefly of silica with a little alumina and oxide of iron; and was evidently derived from small particles of brick and ashes swept up along with the fume. The

carbonaceous matter in No. III. was, doubtless, derived from the fuel, coke, used in the slag-hearth.

I. From the reverberatory furnaces. Colour light reddish-grey. The fume analysed was from a sample made from portions of the fume taken at different distances out of the main flue, into which the short flues from the smelting reverberatory furnaces entered, commencing at a distance of about 10 yards from the furnaces and at regular intervals for about 50 yards: it was unmixed with any other fume. The distance of the stack from the furnaces was about 90 yards.

II. From the bottom of the stack. Colour light-grey with a pinkish tinge. The fume analysed consisted of the mixed fumes of the smelting-furnaces and slag-hearth.

III. From the slag-hearth. Colour dark-grey with a brownish tinge. It was exclusively from the fume produced by the slag-hearth, and was taken from its flue before the latter joined the main flue.

The proportions of sulphuric acid required to combine with the oxides of lead, zinc, and calcium and form PbO,SO^3—ZnO,SO^3—CaO,SO^3, respectively, are as under :—

Sulphuric Acid Required.	I.	II.	III.
For Protoxide of lead	16·69	22·33	16·81
" Oxide of zinc.....	1·61	1·61	4·15
" Lime	8·67	5·39	9·61
	26·97	29·33	30·57
Sulphuric Acid Found	26·51	25·78	14·15
Deficiency	0·46	3·55	16·42

Analyses of lead-fume from Pontgibaud by Rivot.—Several specimens of fume collected at the Pontgibaud Smelting Works (see p. 338) have been analysed by Rivot, who gives the following not very satisfactory account of the system of condensation which was in use there at the time. First, it is stated in a foot-note, that "in order to condense the fumes of all the furnaces of the works, a fan and a great chimney have been erected; the gases and the fume are exhausted by the fan, and pass under a shower of cold water before reaching the chimney."[1] The gases and fumes, we are next informed, pass into a condensing-chamber; and thence into a second chamber, communicating with the fan and great chimney by a subterraneous culvert. If needed, the gases and fumes may escape from a special chimney (p. 143). In a second foot-note (p. 143) the two chambers are said to have been united into one. In a third foot-note (p. 167) it is added that "from the greater richness in silver of the fumes of the fan, no certain inference can be drawn, because the fan exhausts the fumes from cupellation and roasting at the same time as those

[1] Description des Gîtes Métallifères, 1851, p. 142.

from the blast-furnaces." The results are especially interesting as shewing how large a quantity of silver may exist in the fume.

COMPOSITION OF LEAD-FUME FROM PONTGIBAUD.

	I.	II.	III.
Protoxide of lead	—	66·5	3·7
Sulphuric acid	—	17·0	—
Carbonate of lead	35·0	—	—
Sulphate of lead	39·0	—	13·0
Lead	—	—	55·0
Sulphur	—	—	8·9
Sulphide of lead	4·5	—	—
Oxide of iron	—	3·0	13·0
Oxide of zinc	2·7	12·0	3·1
Sulphate of zinc	2·3	—	—
Arsenious acid	1·5	1·1	—
Arsenic (?)	—	—	1·5
Residue insoluble in acids	13·2	—	—
	98·2	99·6	98·2

The analyses are here presented just as tabulated by Rivot.

I. From the roof of the first condensing-chamber. Fume white, flocculent, and tolerably light. 100 kil. of fume yielded, by dry assay, 52 kil. of lead and 129 gram. of silver. 100 kil. of lead, therefore, contained 0·248% of silver. Rivot remarks that "as the temperature is tolerably high in the chamber, it is not astonishing that the fumes should be completely oxidized." It is not easy to explain the formation of carbonate of lead in this chamber, through which sulphurous acid along with some sulphuric acid must have been flowing uninterruptedly for considerable periods.

II. From the roof of the first condensing-chamber. The fume is reported to be white in this chamber, grey in the subterraneous culvert, and nearly black in the fan-chamber (*la chambre du ventilateur*). The specimens in Nos. I. II., it will be observed, came from the same chamber (see pp. 155 and 166), yet the two analyses appear in different parts of Rivot's treatise and differ widely from each other.

100 kil. of fume yielded, by dry assay, 56 kil. of lead and 21 gram. of silver,
100 kil. of lead, therefore, contained ..... 0·050% of silver.

III. The fume, which was nearly black, came from the fan chamber; and as far as I can gather from Rivot's description, the fume from the cupellation-furnace passed only through that chamber in its way to the chimney. If so, the analysis indicates the composition of a mixture of fumes from the roasting, smelting, and cupellation-furnaces.

100 kil. of fume yielded, by dry assay, 62 kil. of lead and 55 gram. of silver.
100 kil. of lead, therefore, contained..... 0·088% of silver.

ANALYSES BY BERTHIER OF AGGLOMERATED LEAD-FUME FROM ALSTON MOOR AND CONFLANS IN SAVOY, NOW BELONGING TO FRANCE.[2]

	I.	II.
Sulphide of lead	1·4*	—
Sulphate of lead	65·6	39·0
Oxide of lead	10·2	42·6
Oxide of zinc	13·8	—
Oxide of iron	3·4	—
Silica and alumina	5·6	17·4
	100·0	99·0

* Particles of slime-ore carried up by the blast or draught?

I. In the statement in his 'Essais,' Berthier omits sulphide of lead. The substance operated upon was agglomerated fume, which "must have been in a state of softness bordering upon liquidity." It was full of rounded cavities, very heavy, even in fracture, dull, and light-grey, with a yellowish and reddish tint. In the 'Essais,' it is reported to have been derived from reverberatory furnaces exclusively; whereas in the 'Voyages' we are informed that at Alston Moor "the smoke from *all* the furnaces [the adjective *all* necessarily including ore-hearths, which are referred to in the text immediately preceding], were conducted into a long chimney."

II. From reverberatory furnaces at Conflans, in which nearly pure galena was smelted. It is described as compact, opaque, even in fracture, and yellowish; and was regarded as a basic sulphate of lead which had been melted.

Particular variety of fume from the blast-furnaces at Pontgibaud.—Analysis by Berthier.[3] Coke was the fuel employed. There was formed a large quantity of black powder which had to be taken out every two or three days through the charging-holes. It consisted of the débris of coke and metallic grains. It was washed, roasted, and smelted along with other matters.

COMPOSITION OF THE WASHED POWDER.

Metallic lead	30
Oxide of lead	6
Sulphide of lead	31
Metallic zinc	23
Iron and sulphide of iron	5
Carbon, etc.	5
	100

It yielded by dry assay 50% of lead and only 0·02% of silver. From this small proportion of silver, Berthier reasonably inferred that the powder was a true sublimate, condensation having taken place at the upper part of the furnace. That this may occur is shown by the

[2] Voyage Métallurgique en Angleterre, par MM. Dufrénoy, Elie de Beaumont, Coste et Perdonnet, 1839. 2. p. 658. Berthier, Tr. des Essais, 2. 744.

[3] Tr. des Ess. 2. p. 745.

fact that small beautiful cubical crystals of sulphide of lead have been found condensed on pieces of coke, at the top of a Spanish slag-hearth. Berthier adds that the volatility of the lead is considerably increased by the presence of zinc.

ANALYSES OF FUME FROM CUPELLATION-FURNACES BY BERTHIER.[4]

	I.	II.	III.
Oxide of lead	88·2	40·0*	71·2
Sulphate of lead	—	20·0	17·8
Oxide of antimony	4·4	—	
Arsenic acid	0·3	3·0	—
Silica and clay	3·4	20·0	4·6
Carbonate of lime	3·7	17·0	—
Carbonic acid	—	—	5·0
	100·0	100·0	98·6

* Inclusive of carbonic acid.

I. From Pontgibaud. Deposited upon that part of the roof of a German cupellation-furnace, which is contiguous to the litharge-channel; it was in the state of powder of a dirty yellow colour.

II. Also from Pontgibaud. Taken from the interior of the furnace; it occurred as white powder. The portion of oxide of lead not existing as sulphate is reported to have been present as carbonate.

III. From the cupellation-furnaces at Villefort, Lozère. The oxide of lead was almost entirely in the state of carbonate.

On the presence of gold as well as silver in lead-fume.—Several specimens have been examined in my laboratory by Smith with a view to ascertain whether one or both of these metals might be present, and in every case, not only has silver been detected but gold also in minute proportions.

Remarks.—Fume, properly so-called, is the product of the sublimation of lead or certain of its compounds; but the deposit to which the term fume is commonly applied, is chiefly composed of true sublimate and in part of the finely-divided matter carried over mechanically by the gaseous current flowing with a pretty high velocity through the furnaces. Both sulphide of lead and metallic lead volatilize at temperatures existing within the furnaces, reverberatory as well as blast; and as galena decrepitates much when quickly heated to redness, the former may also be carried away in suspension in the gaseous current above mentioned. The same may be said of protoxide of lead. Sulphate of lead may, as has been previously demonstrated, be wholly dissipated at a white-heat, while at a lower temperature it is resolved into a basic salt with the evolution of sulphuric acid, sulphurous acid, and oxygen (see p. 41); but it seems improbable that any sensible proportion of fume should be derived from that source. Sulphuric acid would also result from the action of silica upon any sulphate of lead pro-

[4] Tr. des Ess. 2. p. 744.

duced in the process of smelting. There is no difficulty in accounting for the existence of so large a quantity of sulphate of lead as indicated in the foregoing analyses; for that salt would be formed by the long-continued exposure of any sulphide and protoxide of lead, conveyed from the furnaces, to the action of the sulphurous acid which is copiously evolved in the air reduction process and is continually flowing towards the stack. Sulphite of lead would under such conditions be first produced, and then gradually changed into sulphate, more or less completely, by the action of the oxygen of the atmospheric air which is always present in notable proportion in the gases escaping from furnaces in the smelting of galena. That sulphite of lead is formed, at least when refinery-fume containing oxide of lead is present, is certain, as it may be detected in the fume obtained from condensers in which the smoke is compelled to pass through water. The water which escapes from Stagg's condenser smells like a saturated aqueous solution of sulphurous acid. As a little sulphuric acid may also be a constituent of lead-smoke, it likewise would act upon the fume and generate sulphate of lead.

Quantity of fume obtained in smelting lead ores, and in certain other metallurgical processes connected with lead.—I have found but few trustworthy observations on this subject, and I certainly expected, that from some of the great German smelting works where so much care is taken to procure minute and accurate details concerning the quantities of the various products obtained, more information would have emanated on the proportion of lead volatilized and the fume condensed in the smelting of lead ores and in certain other metallurgical processes connected with lead. I have, however, failed to discover such information in the numerous treatises and journals to which I have had access.

The quantity of lead produced from the ore and slag-hearths at the Keld Head Mining Company's Smelting Works from June, 1856, to June, 1857, was 1374 tons; and the quantity of lead extracted from fume during the same period was 96 tons 13 cwt., *i.e.* in the ratio of 14·21 : 1, or 100·00 : 7·03.

The quantity of hard lead extracted from the fume deposited in smelting 78,008 cwts. of *ore* in ore-hearths in certain smelting works in the north of England amounted to 500 cwts., *i.e.* in the ratio of 156·08 : 1, or 100 : 0·64, or (estimating the assay produce of the ore at 77%) as 100 of lead : 0·83.[5] The condensing arrangement consisted of the long horizontal chimney.

In an establishment in the North, ore, containing 73% of lead by assay, produced per 100 tons in the ore-hearth 60·0 of lead, exclusive of 3·2 extracted from the accompanying ore-hearth slag; and 6·91 from the fume collected, *i.e.* in the ratio of 9·15 : 1 or 100 : 10·93.[6] Although not distinctly stated, yet it may be presumed that the fume

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[5] Pattinson, Oct. 1831. Trans. of the Nat. Hist. Soc. of Northumberland, Durham, and Newcastle-upon-Tyne, 1832, 2. Part I. p. 166.

[6] Mr. J. A. Phillips. Lecture read before the Society of Arts, April 27, 1859.

was collected in the long horizontal chimney. Mr. J. A. Phillips estimates that in well-constructed flues, the fume deposited yields from 2% to 3% of the lead contained in the ore; but, it will be perceived that this statement does not agree with the preceding data of Mr. Phillips, with respect to the proportion extracted from ore-hearth and slag-hearth fume.

According to Stagg, the following quantities of lead were extracted from the fume, collected by means of his condenser, per 100 tons of lead obtained from smelting in the ore-hearth, in the reverberatory furnace, in the slag-hearth, and in the operations of cupellation and reducing respectively :—[7]

Ore-hearth,	100 tons of lead	:	5 tons of lead.
Reverberatory furnace,	,,	:	4 ,,
Slag-hearth,	,,	:	20 ,,
Cupelling and reducing,	,,	:	7 ,,

Fallize has recorded the following results of two experiments on the large scale, which, he states, were made with the greatest care in 1859, without mentioning the locality.[8] In both experiments the smelting was conducted in a blast-furnace; but in one *raw* ore was operated upon, and in the other the same ore *roasted*. The nature of the furnace charge is not given.

Nature of the ore subjected to treatment.	Percentage of lead in the ore, calculated from the numbers in the next column.	Weight of ore treated in kilogrammes.	Weight of lead in kilogrammes.					Loss due to volatilization, expressed in hundredths of the weights of lead contained in the ores.
			In the ore.	Yield.	Loss.	In the poor slags thrown away.	In the fume.	
Raw ore	50·86	32,000	16,276	13,430	2846	808	2038	12·52
Roasted ore ...	65·43	36,115	23,630	21,269	2361	542	1819	7·69

The weight of the lead carried away in the smoke during the roasting of the ore, which amounted to 2·78% of the lead contained in the raw ore, is included in the number 7·69 in the last column. According to Fallize on the average in lead-smelting the lead carried off in the smoke amounts to 10% of the assay produce of lead in the ore, a statement which is opposed to the experience of this country; and, while in lead works where rich galenas are smelted in reverberatory furnaces, the quantity volatilized may be less, yet Fallize puts the question, in how many others does it not exceed that proportion? The answer which I have received to this question from an experienced and authoritative source is, "in none in England,

[7] Richardson, Watts' Chem. Dict. 524. At certain lead-smelting works, where Stagg's condenser has been applied, only about half of these proportions of fume has been collected.

[8] Revue Universelle, 1862, 11. 372.

unless it be in some little work where old slags and other residues are smelted, and there the loss is only in part through volatilization."

Treatment of lead-fume.—The analyses of lead-fume evolved from blast as well as reverberatory furnaces, prove that for the most part it consists of sulphate of lead; and, therefore, the problem involved in its treatment is simply the reduction of that salt. But that problem, it will be remembered, has been previously examined in considering the treatment of *grey-slags*, which contain a notable quantity of sulphate of lead, and of ores of lead in which the metal is either largely or wholly present in the state of sulphate.

Owing to the powdery state of the fume, it has been found convenient to agglutinate it into lumps, which may be done in two ways, namely, by heating it in a reverberatory furnace to a degree sufficient to soften it and cause its particles to clot together; or, by mixing it with cream of lime and then leaving the mixture exposed to the atmosphere until it becomes hard, after which it is broken into pieces of convenient size for charging. Especially is this preliminary treatment desirable, when it is intended to reduce the fume in a blast-furnace of any kind; for, notwithstanding the large proportion of lead which it contains, its particles are so fine and mobile that in a blast-furnace, particularly one of low dimensions, much of it might be blown out and escape with the gases omitted from the mouth. The fume is either treated by itself or in conjunction with various residuary products obtained in the smelting of lead and processes connected therewith. Thus, it may be smelted, in the flowing-furnace along with *grey-slags*—in which case no preliminary agglomeration would be required—iron in this case being used as an accessory, though, it is affirmed, not a necessary, agent of reduction; or it may be smelted in conjunction with such slags in the slag hearth or other blast-furnace. In the former case iron-slags are sometimes added, chiefly with the object of producing a more liquid slag, as the slag resulting from the smelting of flue-dust alone is apt to be deficient in liquidity, especially when it contains much lime. In the North, fume is smelted in the common slag hearth, having been previously heated so as to make it cohere into lumps. The 500 cwts. of slag-lead referred to at p. 289 were obtained in this manner. In recent times, in Flintshire, fume has been mixed with the crushed *grey-slag* used in the smelting of silver ores.

SOFTENING OF HARD LEAD.

The terms calcining and improving are used as synonymous with softening. Lead, as it comes from the smelting furnaces, is often so contaminated with impurities as to be too hard and deficient in malleability to admit of being applied to various manufacturing purposes; and it has therefore to be subjected to further treatment to render it marketable. Moreover, the same may be stated with respect to its suitableness for Pattinson's process of desilverization, only comparatively pure lead being adapted for that process. The quality of the lead

depends less upon the mode of smelting than on the quality of the ore from which it is derived.[1] While some ores are so free from those foreign matters, which communicate hardness, as to directly yield soft and good lead, others are associated with such matters, notwithstanding most careful dressing on the part of the miner, in such a degree that the lead from the smelting-furnace is hard and bad. The composition of various kinds of lead will be found in the descriptions of the respective processes of lead-smelting and elsewhere in this volume.

Softening Hard Lead by Atmospheric Oxidation.

The process of softening hard lead has for its object the separation of foreign matters upon the presence of which the quality of hardness depends. These matters are capable of oxidation at a red-heat, especially in conjunction with lead; and antimony, the chief culprit, having, when in the state of oxide, a pretty strong affinity for protoxide of lead, its oxidation is greatly promoted by virtue of that affinity, as, for example, in the case of exposing lead alloyed with antimony to a red-heat with free access of atmospheric air (see p. 87). On this principle the usual process of softening hard lead is founded. The metal is kept melted, say at a dull red-heat, with a current of atmospheric air flowing over it. For this purpose a reverberatory furnace may be used, having a bed made of suitable material and so constructed as to prevent the percolation and escape of molten lead. The dross which is formed is from time to time skimmed off, and the operation is prolonged until the residual lead is found on trial to have acquired the proper degree of softness. Just as in the process of refining blister-copper, it is necessary to oxidize a considerable quantity of copper in order to separate its impurities, so in the softening—or as it might strictly be designated refining—of hard lead, it is also necessary to oxidize a considerable quantity of lead.

Softening furnace with cast-iron bottom.—A reverberatory furnace with a cast-iron bottom, exactly similar in all respects to that described at p. 150 as used in the treatment of lead desilverized by zinc, is well suited for the softening of hard lead by atmospheric oxidation, and is accordingly employed for that purpose. The process is conducted in the case of ordinary hard lead precisely as stated in the description of the method of desilverization by zinc.

According to Mr. J. A. Phillips, the cast-iron bottom of a softening-furnace at the Pontgibaud Smelting Works, where he formerly officiated as manager, is 13′ long by 6′ 6″, outside measure [the depth is not given]; it is dish-shaped in section and rounded at the angles with the view of lessening its tendency to crack; and is set on a bed 2′ thick of solid brasque, which rests on a solid foundation of

[1] In the smelting of poor impure ores, whether by the Cornish method or in blast-furnaces, all the lead is separated at once, and it may be regarded as equivalent to a mixture of the soft and slag-lead, which are obtained from rich ores in England by two processes, and are kept apart.

masonry; there is a tap-hole $\frac{3}{4}''$ in diameter at the lowest part of the bottom, communicating with a thick cast-iron pipe fastened to it by stud-bolts screwed into the metal to the depth of about $\frac{1}{2}''$; the cast-iron pipe at the opposite end protrudes beyond the furnace. Before charging, the tap-hole is plugged by inserting the point of a long iron bar through a hole in the roof immediately over it. This bar, Mr. Phillips says, will not generally stop the tap-hole quite tight, especially after the furnace has been working a long time. The cast-iron pipe is partly filled with bone-ash firmly rammed in, a bar of iron having been previously placed in the pipe so that the channel left after its withdrawal may correspond with the tap-hole in the bottom. This horizontal bar is said to be more necessary than the vertical one; by means of the latter the outflow of the metal in tapping may be regulated. "The sides of the furnace," it is stated, "must be either of thick iron [cast-iron?] plates, or of large cut stones. In either case the space between them and the pan should be at least 1′ wide, and well filled with hard beaten brasque." There are two working-doors, and both on the tap-hole side. Two furnaces of the kind above described were erected, one for common lead and the other for lead reduced from dross; "the former has been almost constantly in use for upwards of 5 years; and although the pan is now cracked, the furnace is as tight and serviceable as ever." The usual charge for one furnace is about 20 tons of Pontgibaud furnace-lead, and it requires about 60 hours to render the metal sufficiently soft for treatment by Pattinson's process, or 3 days inclusive of the time expended in charging and discharging. The percentage of soft lead obtained is stated to be about 94·7. The cost of softening is reported to be 3*s.* 4·8*d.* per ton of common furnace-lead (*i.e.* obtained by smelting the ore in a blast-furnace, see p. 338), or 1*s.* 6·2*d* per ton of ore.[2]

In Freiberg, softening is effected either in a reverberatory furnace with a cast-iron bottom, or in a reverberatory furnace similar to but of smaller dimensions than that described and figured in the article on lead-smelting at Freiberg. Oxidation is aided by artificial blast which enters through two twyers, one on each side of the fire-bridge. The lead is slowly melted down, and the scum which collects on the surface and in which the copper becomes concentrated, is raked off; after which the process is continued with a gentle blast, the impure litharge or *Abstrich* being constantly removed, until the residual lead has become sufficiently pure. Indications of the requisite degree of purity of the softened lead are afforded by its malleability, its behaviour when heated before the blowpipe on charcoal, and by its specific gravity. Samples are taken out of the furnace in order to be examined with respect to those points. Arsenic may be recognised by its characteristic odour when about 2 grammes are put into a little hollow in a piece of charcoal and melted rapidly in the reducing

[2] The Mining and Metallurgy of Gold and Silver. By John Arthur Phillips, Mining Engineer, 1867, pp. 482 *et seq.*

flame and kept heated during a few seconds. Antimony by the same means may be detected by the blueish-white incrustation of oxide of antimony which is formed. The presence of both is shown on the solidification of the globule of lead by the absence of its characteristic lead-grey colour, by the dulness of its surface, and by its coating of dark-grey litharge.[3]

Mode of charging.—The lead may be introduced in pigs or laded in from an adjoining cast-iron pot seated over a fire-place and kept filled with molten lead. Richardson has described what he designates as an improvement in the mode of charging, which is as follows, and which is only described here as a warning to avoid what is useless. A large flanged cast-iron pot, like those used in the Pattinson process of desilverization, is fixed immediately over the furnace, so that the centre may be a little beyond the side of the fire-bridge furthest from the fire-place, of which that side inclines steeply towards the bed. It is set in brickwork encased in a cylinder of iron plate. As far as I can interpret Richardson's woodcuts, illustrative of this arrangement, there is a hole in the roof of the fire-place through which flame rises, and after coursing round the sides and bottom of the pot is expected to descend through the roof of the body of the furnace at some distance from the fire-bridge. In the bottom of the pot is a round hole, to which is attached an iron pipe descending vertically through, but not beyond, the roof near the top of the inclined side of the fire-bridge. In the axis of the cast-iron pot is a vertical iron rod, plug-shaped at the bottom and tapped with a screw thread at the top, which passes through a transverse flat bar of iron fixed at a convenient height above the pot. A handle with a female screw works on the top of the rod, which may thus be raised or lowered at will so as to drop in and completely close the hole in the middle of the pot at the bottom. The pot is kept filled with melted hard lead, which on raising the rod above-mentioned drops into the furnace. Richardson asserts that "this form of furnace possesses great advantages when softening extra-hard lead, as the calcining pan can easily be kept always full, with very little labour."

Time required for softening.—This will vary with the quality of the lead treated, the surface of the lead exposed to the action of the air, and with the temperature. If the lead is very impure, the dross, according to Richardson, floats in a semi-fluid state on the surface of the molten lead, and must be thickened by intermixture with a little lime before it can be skimmed off; but the same object is usually attained by letting the furnace cool a little.

Poling of softened lead before pattinsonizing it.—At one of the largest lead works in the kingdom, all the softened lead is poled previously to pattinsonization; and the reason alleged for this is, that it is handy to put the scum or froth which is thrown up in poling back into the softening-furnace, where it liquates and saves trouble in

[3] Plattner's Vorlesungen über allgemeine Hüttenkunde, 2, p. 137.

desilverizing. The pot attached to the softening-furnace is large and holds 10 tons. Pattinsonization, however, is stated to be more effective than poling.

History of the process of softening by atmospheric oxidation.—The late Dr. Richardson, of Newcastle-on-Tyne, seems to have imagined that he was the inventor of this process. In an article on lead written by himself the following passage occurs.[4] "The writer having carefully examined the WB (*i.e.* William Blackett) slag-lead, found that its hardness was mainly due to the presence of antimony. He then suggested the erection of furnaces in which this lead, in a melted state, could be exposed to a current of hot air. The result was the production of a good soft lead, at so reasonable a cost as to render the process available as a regular operation in smelt mills. Soon afterwards, the first cargoes of the now well-known Spanish hard lead arrived at Liverpool; but the smelters there would not purchase them, and one cargo was transhipped to Newcastle-on-Tyne. This lead could not be softened in the brick furnaces, being so fluid when melted as to find its way out of the furnace in all directions. [This is a surprising statement, seeing that at some British lead-smelting works brick furnaces alone are used in softening Spanish hard lead.] The late Mr. G. Burnett, who consulted the writer on the subject, and witnessed the treatment of the slag-lead at Mr. Beaumont's works at Blaydon, then proposed the simple but admirable plan of lining the furnace with a metal pan. Thus was laid the foundation of a trade with Spain, which has gone on increasing, until, it is said, upwards of 20,000 tons of this description of lead are annually produced in that country."

I have received a letter from my friend, Mr. I. Lowthian Bell, enclosing a note to him from Mr. James Leathart, dated Lead Works, Newcastle-on-Tyne, Dec. 3, 1867, in which is the following passage: "As to the introduction of the present mode of 'softening,' as you know, the late Dr. Richardson had no more to do with it than the 'man in the moon.'"

A patent was granted to Walter Hall in 1816 for "A method or methods of making soft lead out of hard lead or slag-lead." The calcination of hard or slag-lead in the process of making red-lead was continued until it was found that the residual unoxidized lead had become soft. In the charge of about 20 cwts. of hard or slag-lead, $3\frac{1}{2}$ to 5 cwts. might be calcined, and the remainder withdrawn as soft lead.[5] It must have been *very, very* hard lead.

The specification just quoted proves conclusively that the invention of softening lead by the joint action of atmospheric air and heat did not originate with Dr. Richardson. But to go further back. What is the German method of cupellation in the early stage but the softening process? First after fusion of the lead the *Abzug* rises

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[4] Watts' Dictionary of Chemistry, 1865, p. 516.

[5] A. D. 1816. Nov. 21. No. 4085. Abridgments of the Specifications of Metals and Alloys, p. 47.

to the surface and is removed; and then follows the *Abstrich* or litharge containing the identical impurities, which are the usual causes of hardness in lead. In the English process oxidation is effected in a reverberatory furnace at a temperature above or below the melting-point of litharge, according as the furnace-bottom is made of slag or of cast-iron, whilst in the German process of cupellation atmospheric oxidation takes place above the melting-point of litharge and an artificial blast is employed. In the early stage of the latter process the chemical phenomena are essentially the same as in the former.

Bishop Watson published the results of experiments which he made, with a view to ascertain the order of succession of the colours in the iridescent pellicle which appears on the surface of lead when melted; and had those results attracted the attention of lead-smelters of his day, the process of softening by atmospheric oxidation would probably have soon afterwards come into general use, that is, assuming that in Watson's day there was any considerable quantity of hard lead which it was desired to soften, which was probably not the case. This is Watson's own account of his experiment: "The lead which lines the boxes in which tea is imported from China happening to be at hand, some of it was melted in an iron ladle; but I was much surprised to find that its surface, though it was presently covered with a dusky pellicle, did not exhibit any colours. Imagining that the heat was not sufficiently strong to render the colours visible, the fire was urged till the ladle became red hot, the calcined pellicle upon the surface of the lead was red hot also, but it was still without colour. The same parcel of lead was boiled in a crucible for a considerable time; during the boiling a copious steam was discharged, and the surface of the lead, as is usual, became covered with a half vitrified scoria. The lead which remained unvitrified was then examined, and it had acquired the property of forming a succession of coloured pellicles, during the whole time of continuing in a state of fusion. Another portion of the same kind of lead was exposed to a strong calcining heat for a long time; the part which remained uncalcined did, at length, acquire the property of exhibiting colours sufficiently vivid."

From the foregoing results Watson inferred, that Chinese tea-lead was mixed with something which prevented the formation of an iridescent pellicle, and which by calcination was removed. He made numerous experiments with a view to discover what that something might be, and arrived at the conclusion that it was tin. He found that on putting a small portion of tin into a ladle full of molten Derbyshire lead which exhibited the usual colours, these disappeared as soon as the tin melted; and as to the proportion of tin required to produce this effect, he writes, "I have reason to believe, that it does not exceed one five-thousandth part of the weight of the lead." The Derbyshire lead, which had lost its property of exhibiting colours on the addition of tin, acquired it again by calcination, "the tin, it is supposed, being separated from the lead by calcination, before all the lead is reduced to a calx."

Calcined Chinese tea-lead was heated with tallow and the reduced lead exhibited colours; from which it was concluded that the supposed intermixed calx of tin (SnO^2) had remained unreduced by the tallow. Zinc was found to have the power of depriving lead of its property of exhibiting colours, but not in so great a degree as tin. The addition of small portions of bismuth to lead did not prevent the formation of coloured pellicles;[6] nor did the addition of silver. But a little tin added to a mixture of lead and bismuth, or of silver and lead, immediately prevented the appearance of colours.[7] It may be added that tea-lead, subjected to atmospheric oxidation, yields, according to Richardson, 76·4% of lead free from tin.[8]

Softening of Hard Lead by Special Agents of Oxidation.

A patent was granted to Messrs. Pontifex and Glassford, in 1854, for softening hard lead by adding to the molten metal, when containing from 5% to 15% of antimony, a mixture of 3 parts (by weight) of nitrate of soda, 4 parts of soda-ash, and 4 parts of caustic lime. When the hard lead contains less than 5% of antimony a mixture composed of equal parts of the three ingredients above mentioned may be used. The process is conducted in an ordinary softening-furnace. The mixture is sprinkled at intervals on the surface of the molten lead, which is skimmed at intervals as usual. From 40 to 60 lbs. of the mixture may be employed with 9 or 10 tons of lead. The dross may be reduced in the common way, or it may be treated with boiling water, which, it is stated, will remove all but oxides of lead and antimony. Part of the oxide of lead may be dissolved out of this residue by nitric acid, when a crude Naples yellow is left, from which metallic antimony cannot, as stated, be prepared.[9]

Richardson in 1852 obtained a patent, in which he claimed, amongst other things, the preparation of sugar of lead by the solvent action of acetic acid upon the dross produced in the softening of hard lead.[10] But it dissolves out only uncombined oxide of lead, and there remains combined oxide in notable quantity. In 1847 A. H. Johnson obtained a patent for the use of acetic acid as an agent for dissolving out the oxide of lead in old cupels or test-bottoms. The cupels are reduced to powder and mixed with sufficient pyroligneous or acetic acid (of sp. gr. from 1·030 to 1·048) to form a thin paste, which is stirred and left to settle during about two days, when the bulk of the oxide of lead will have been dissolved. The residual bone-ash, containing silver and very little lead, may be used again after having being strained, washed, and dried. Acetic acid may be

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[6] A lead-smelter informs me that he thinks bismuth increases the brilliancy of the colours rather than otherwise.

[7] Chemical Essays, 1782, 3. pp. 242 *et seq.*

[8] Op. cit. p. 518.

[9] A.D. 1854. July 26. No. 1644. The title is "Improvements in obtaining soft lead from hard lead, for the separation of the impurities in hard lead, and for the separation of antimony from these impurities." Abridgments of Specifications of Metals and Alloys, p. 271.

[10] A.D. 1852. April 28. No. 14,093. Op. ant cit. p. 199.

replaced by a solution of caustic potash or soda, containing about 20% of pure alkali.[11]

In 1860 a patent was granted to Warner for softening hard lead by immersing in the molten metal a box containing oxidizing agents, such as nitre.[1]

In 1860, Mr. W. Baker, of Sheffield, procured a patent for the use of the following agents in the softening of hard lead: alkaline nitrates or chlorates,—hypochlorites of the alkalies and alkaline earths,—sulphate of iron,—and a mixture of bisulphate of potash and common salt.[2] In Baker's experiments with these substances he stirred them "vigorously into the melted lead, kept at a suitable temperature." He found nitrate of soda to answer exceeding well, as it operates upon lead heated only to dull redness. After the action is over, dross rises to the surface of the molten lead, which, after having been skimmed clean, presents the iridescence characteristic of soft lead. Baker tried the peroxides of manganese and lead, but without success, owing, it was supposed, to the evolution of oxygen from them at a lower temperature than was required for the oxidation of the impurities present, which, in the lead treated, were chiefly sulphides of lead and antimony. The metal subjected to experiment by Baker was Derbyshire slag-lead, of which several samples were analysed by him, and the mean percentage of impurities found to be as under:—

DERBYSHIRE SLAG-LEAD.

	Per Cent.
Sulphur	0·346
Antimony	0·132
Copper	0·071
Iron	0·021

Small particles of black-slag and traces of other impurities besides those above enumerated were usually found in slag-lead. The proportion of sulphur exceeds what is required to combine with the antimony, copper, and lead, and the excess is rightly assumed to be in combination with lead.

In the foregoing experiments the iron, which is stated to have been chiefly present as sulphide mechanically diffused through the lead, was reduced from 0·050% to 0·009%. The first number is, it will be observed, larger than that given above. The copper, contained in the lead, was not removed in the least degree. According to Baker, this process of softening "is specially adapted to those localities where the lead contains very little silver and not much antimony. If it contain much antimony [or little?] the cost of oxidizing it [the latter] away will not compare with the slow method of roasting in the improving furnace, as practised at the lead-works where silver and antimonial leads are worked up."[3]

[11] A. D. 1847. Sep. 23. No. 11,872. Abridgments of Specifications of Metals and Alloys, p. 153.

[1] Watts' Dict. of Chemistry, 3. p. 530.

[2] Ibid. 3. p. 530.

[3] Letter, signed William Baker. Mining Journal, March 2, 1861.

Treatment of Dross obtained in Softening.

The dross or oxidized product of the softening process may be reduced by heating it in admixture with carbonaceous matter either in a reverberatory or blast-furnace; and the metal yielded, which for the sake of distinction may be termed *second* hard lead, may be subjected to atmospheric oxidation in a softening-furnace. Supposing the reduction of the dross to be complete and no sensible loss during reduction to arise from volatilization, this *second* hard lead must contain a larger quantity of foreign metallic matter, such as antimony, than the *first* or original hard lead; and much more dross must be formed than in the process of softening that lead. Indeed, this second dross may contain so much antimony as to be incapable of further economical treatment as a source of soft lead. It may, however, be used for bullets and for inferior type-metal, or in some cases converted into a pigment (see p. 87). Richardson states that in one case which came under his observation, 30 days were required for the softening of lead reduced from the dross of previous operations.[4] The same authority recommended, that in the reduction of dross by heating it with admixture of coal in the reverberatory furnace, as is usual, about 2½% of soda-ash should be added along with the coal; and the reasons assigned for such addition are, that the slag is thereby rendered more fusible, and the workman is enabled to work at a lower temperature. He gives the following analyses by himself of the lead reduced from dross without (No. 1) and with (No. 2) the addition of 2½% of soda-ash:—

	I.	II.
Lead	82·88	58·70
Antimony	16·09	40·66
Copper	0·68	0·32
Iron	0·35	0·32
	100·00	100·00

All that can be deduced from these data is that soda-ash caused a relative increase in the proportion of antimony reduced. By repeating the calcining operation on the produce of the reducing-furnace, and reducing the resulting dross with the addition of soda-ash, the metals obtained were found [by Richardson] to possess the following composition:—

English Hard Lead.

	I. Original Lead.	II. Lead from Dross of 1st Calcination.	III. Lead from Dross of 2nd Calcination.
Lead	99·27	86·53	52·84
Antimony	0·57	11·29	47·16
Copper	0·12	traces	traces
Iron	0·04	0·34	traces
	100·00	98·16	100·00

[4] Op. cit. p. 519.

Spanish Hard Lead.

	IV. Original Lead.	V. Lead from Dross of 1st Calcination.	VI. Lead from Dross of 2nd Calcination.
Lead	95·81	64·98	56·60
Antimony	3·66	29·84	43·40
Copper	0·32	5·90	traces
Iron	0·21	0·20	traces
	100·00	100·92	100·00

It was found impossible to separate any soft lead from Nos. III. and VI., by subjecting them to the softening process, as all the metal became oxidized.[5] The expense of reducing the dross, per ton of lead yielded, exclusive of repairs, is given as under:—

	s.	*d.*
Labour	5	2·1
Coal	1	3·2
Soda-ash	2	1·5
	8	6·8

The process was conducted in an ordinary reverberatory reducing-furnace of smaller dimensions than usual; and we are informed, that this was because the "charges are smaller and require more attention to prevent the loss of antimony by volatilization." Most lead-smelters, it may be presumed, would be well satisfied to have the whole of the antimony volatilized!

Liquation of Hard Lead.

The state and proportions in which antimony and some other metals exist in hard lead are such as to admit of the partial separation of those impurities by a process of liquation, which, however, can only be regarded as preliminary and subsidiary to softening, properly so called. The following observation communicated to me concerning hard lead reduced from dross obtained as the ultimate product of several successive calcinations and reductions, will show how, by crystallization, a definite alloy may separate from a mixture of molten metals. About 10 tons of such hard lead, containing silver, were melted in a Pattinson-pot and skimmed clean on Saturday evening, fire being left under it. On the Monday following, on re-melting the metal in the pot, which had partially set, a crystallized crust of about 3″ in thickness, appeared at the surface, which evidently consisted of metal less fusible than that underneath, from which it had separated. On raising this crust, the liquid alloy drained out very completely, and left a cake of very large and brilliant interlacing crystalline plates.

The most largely crystalline and foliated portion of this crust has been analysed in my laboratory by Mr. Ward, and not a little diffi-

[5] Op. cit. p. 519.

culty was experienced, as the usual methods of analysis prescribed for a substance containing lead, antimony, tin, and arsenic were not found to be accurate.

CRYSTALLINE ALLOY.

		Ratio of equivalents.	
Lead	57·83	0·556	
Tin[6]	9·40	0·162	
Copper	2·44	0·076	0·831
Iron	0·18	0·006	
Nickel	0·89	0·031	
Antimony	27·55	0·230	
Arsenic	0·62	0·008	0·270
Sulphur	0·52	0·032	
	99·43		

Electropositive elements ..... 0·831
Electronegative elements, 0·270 × 3 = 0·810

The following formula would, therefore, represent the composition of this alloy:

$$3(PbSnCuFeNi) + (SbAsS).$$

From the foregoing data, the probable inference seems to be that this alloy had been dissolved in the original metal, and separated during slow cooling, rising to the top from its having a lower specific gravity than the subjacent metal; but as it had a higher melting-point than the latter it continued solid after the former had become liquid. Dick informs me that by prolonged contact with the liquid metal, the alloy would not have been re-dissolved, unless the temperature had risen to its melting-point, when one portion would have re-dissolved and another richer in copper would have been left, perhaps along with partially oxidized products: at a red-heat, and in a reducing atmosphere, all would have redissolved. The separation of one or more definite alloys during slow solidification of molten mixtures of certain metals has been rendered exceedingly probable, not to say established, by Rudberg, whose experiments on that subject will be given in a subsequent volume. The mode of existence of silver in a liquid amalgam of that metal and mercury may be more or less analogous to that of the alloy above described in the hard lead when molten; and it would be interesting to learn whether such an alloy might be separated by filtration from the mass of lead, just as silver may be separated by the same means from the mass of mercury in the state of a solid amalgam of definite atomic constitution. Dick considers that on the Saturday it was truly dissolved and could not have been separated by filtration, the temperature at that time exceeding the melting-point of the crystallized alloy. In Pattinsonizing such impure antimoniuretted lead, the crystals which first separate float and may be caught by the ladle. Either tin

[6] The tin was derived from plumber's solder, and was contained in the skimmings from the pipe and rolling-mills.

or copper, especially the latter, is regarded as essential to separation such as that in question. Further:—The separation of a triple alloy of iron, tin, and arsenic, termed "hard head," which occurs in the refining of tin, seems to be another case in point. This alloy is contained in the tin which flows from the furnace when certain ores of tin are smelted, and is apparently in solution in the metallic mass. On heating the solidified tin to, or just above, its melting-point, the triple alloy is left unmelted, while the tin liquates or trickles away. The liquated tin, however, carries off some "hard head," which is subsequently removed by what is designated "boiling" or "tossing." The *modus operandi* of these operations has been investigated in my laboratory, and has, I think, been satisfactorily explained. Further information on that subject will be communicated in an article on the refining of tin. Suffice it in this place to observe, that the so-called operation of *poling*, which is occasionally resorted to after the softening of lead, produces an analogous result in the "boiling" of tin, which is only *poling*. In the article on the desilverization of lead by zinc (p. 152), the process of poling, as conducted in the case of lead, has been described. In poling tin or lead the effect is chiefly the removal of mechanically suspended matter. "Frothy lead" will throw out much "dirt" by poling. "Dirt" is anything suspended in, but *not alloyed* with, lead. At a red-heat this "dirt" will dissolve in lead; but at that temperature poling would not separate it, though it will at a lower temperature.

Liquation and poling at the Silver Works at Schemnitz.[7]—The furnace employed for liquation is similar in construction to the Bleiberg lead-smelting-furnace (see p. 261). Immediately in front of and below the lower end of the furnace, a circular cast-iron pot, like those used in Pattinson's desilverization process, is fixed over a fire-place of its own. An iron gutter is adjusted to that end of the furnace by which molten lead flowing from the latter may drop into the pot. Over the pot is an arrangement by which the lower ends of pieces of wood placed vertically may be kept depressed in the molten lead in the pot. Experiments on this process were first made at Schemnitz in 1860. The lead to be operated upon is subjected to a carefully regulated temperature in the reverberatory furnace, so that it may trickle into the cast-iron pot in drops. Fresh lead is charged from time to time as liquation proceeds. When the whole charge is liquated, the fire under the pot is increased so as to render the lead which it contains thinly liquid. The crust which swims on the surface is skimmed off with a wedge-shaped piece of wood. The pieces of wood above-mentioned are now depressed deep in the metal, and poling is actively kept up for two hours or so, the partially oxidized products on its surface are removed, and when the process has been sufficiently long continued, the surface of the lead will present the characteristic appearance of soft lead. In the pre-

[7] Combinirte Saigerungs- und Raffinirungsmethode des Bleies. H. W. Kachelman. Berg- u. hüttenm. Jahrbuch, 1862, 11. p. 198.

liminary experiments on the process the following analytical results were obtained :—

	Composition per Cent.	
	I. Liquated Soft Lead.	II. Lead after Poling.
Lead	98·954	99·686
Silver	0·005	0·001 [8]
Copper	0·456	0·116
Antimony	0·212	0·089
Iron	0·126	0·010
Zinc	trace	—
	99·753	99·902

After experience had been gained and the process was in regular working order, the lead was found to have the following composition per cent. :—

Lead	99·900
Silver	trace
Copper	0·090
Iron	0·009
	99·999

REDUCTION OF LITHARGE.

The reduction of litharge is effected by heating it in admixture with carbonaceous matter, such as charcoal or bituminous coal, say to the temperature of redness; and for this purpose either a reverberatory or a small blast-furnace may be employed. The choice of furnace will depend upon local considerations, and possibly in some cases upon the prepossessions of the smelter.

Reduction in the reverberatory furnace.—In England, as well as in various localities on the continent, the reverberatory furnace is preferred, in the construction of which there is nothing remarkable. Its bed should slope either towards a tap-hole in the side or at the end. In the tap-hole a gutter of cast-iron is inserted, along which the lead may trickle and be received into a cast-iron pot below. The reduced lead is laded from this pot into ingot-moulds of the usual form and size. The tap-hole is kept closed during the earlier part of the day's work while lead flows freely. The opening in the tap-hole plate, immediately above the tap-hole is partially dammed up with clay, and over the dam so formed the lead runs. Towards the end of the day the tap-hole is opened, and the lead which has been retained in the furnace all day in order to prevent slag from sticking to the tap-hole cavity is let out.[9] It is hardly necessary to remark, that the bed

[8] Too much silver is represented as having gone out, or more than a trace of zinc was present (?).

[9] In very busy times this lead is let out only two or three times a week, but under ordinary circumstances, it is tapped each day, in order to see that the furnace bottom is in good order, and to allow of any "*fettling*" which may be required.

of the furnace should be made as impervious to molten lead as practicable. How this result may be best attained will be found in the descriptions of various lead-smelting reverberatory furnaces in this volume. Towards the end of the last century Jars saw a litharge-reduction furnace at Newcastle-on-Tyne, of which the bed consisted of a layer of bone-ash well beaten down, covered with another layer of clay.[10]

The mixture of litharge and its reducing agent should not be intimate, experience on the large scale having shown that generally the best result is obtained when both are in coarse particles. When coal is used for reduction, the bed of the furnace is covered with a layer of slack a few inches thick, and upon this layer—which, assuming the furnace to have been previously heated, quickly ignites and emits the usual smoky products of the distillation of coal—the charge of litharge intermixed with coal slack in about the proportion required for its reduction is spread evenly over. Metallic lead soon begins to trickle towards the tap-hole and continues to do so uninterruptedly, fresh mixture of litharge and coal being supplied from time to time. Towards the end of a shift, which lasts, say, from 9 to 12 hours, charging ceases, and the slaggy residue is raked out of the furnace. Towards the end of the operation the mass on the bed of the furnace should be rabbled at intervals. The furnace is now ready to be charged again and worked in the manner above described. The residue is called litharge-slag, and contains the ash of the coal with any portions of unconsumed coal, and unreduced residue with, it may be, particles of metallic lead. It is desirable that as little of this slag should be formed as possible; and with that object coal should be selected for reduction which contains least ash. The litharge-slag may be smelted in a small blast-furnace, such as the slag-hearth, described under the processes of lead-smelting.

The following graphic description of the process is from a British smelter. The furnace employed is reverberatory, on the Flintshire model, and should be as large as possible. The opening in the tap-hole plate over the tap-hole is to be partially stopped with clay, so as to form a dam over which lead may flow, and the ordinary tap-hole underneath, it need hardly be remarked, is stopped up. The furnace is made red-hot, and then small coal of best quality is thrown over the bed to the thickness of 2″ or 3″. Whilst this is coking, the charge is to be brought up to the furnace and sprinkled with small coal. The furnace is to be filled as full as practicable, but the tap-hole cavity or well is to be kept empty. This cavity, which holds from 1 to 2 tons of lead, fills rapidly, and while the furnace needs no attention, the bringing up of the charge to the furnace is continued so that it may be ready to be thrown in, for the work will be hard and hot before long. In an hour or two, according to the heat, condition of the charge and other circumstances, the cavity will be full and lead will begin to

[10] Voyages Métallurgiques, 1780, 2. 553.

run over the dam. If there is no fire under the receiving-pot, the dam is to be made higher, so that more lead may accumulate in the well. Charging is continued as the charge in the furnace shrinks, the fresh portion being spread, but the old *not* rabbled. When the cavity is full of lead the last added part of the dam is broken down and the pot will be full in a minute or two of red-hot lead, which warms the ground, and prevents the lead from setting in the pot. Lead will continue to overflow into the pot and must be laded out. The fire is kept up, fresh charges are added, and lading continued, otherwise lead will flow over from the pot, and so on: the work is very hard for 3 or 4 hours, by which time all the charge will have been put into the furnace. With the day of 12 hours the charging should be completed in 6. The work now becomes lighter, as there is nothing to do but lade. When lead ceases to overflow freely, it may be said that no more pure litharge exists: there is residual matter rich in oxide of lead and metallic particles spread through much cinder, but which rapidly wastes and the charge shrinks. *Now* the charge must be rabbled and the fire again urged. More lead will overflow, not quite so good in quality, but still good enough to Pattinsonize. The dam is broken down in part, and lading, rabbling, and firing repeated. Lead ceases to flow from the charge, and then the fire is allowed to go down; but if the residual product is not to be passed through a blast-furnace, the rabbling is continued until most of the cinder is burnt out. The tap-hole is opened to the lowest point, every particle of lead in the pot is laded out, the cinder is drawn, the grate is cleaned, if need be any part of the bed *now wholly exposed* is fettled, the tap-hole is closed, the dam is made up, and all is ready for the next operation. The day's work is good, if the foreman finds the number of pigs sufficient and the cinder satisfactory, which will depend a good deal on the quality of the litharge or skimmings and on the coal. All being good, there should remain little of anything but cinder with here and there shots of metal. If arsenic, antimony, tin, copper, or other metals were present in the litharge, more slag, or what is called "slag," will remain, than if purer litharge had been operated upon: lead, reduced from litharge of good average quality, becomes thick, and what is termed "frothy," before setting; and a pig of such lead gives a very dull sound when struck.

The skimmings from Pattinson's desilverization-pots, or pot-dross, are treated as in the reduction of litharge; and so may the dross produced in the softening or calcining of hard lead. As in a series of Pattinson's desilverization-pots, the skimmings from different pots vary in content of silver, they should generally at least be reduced separately, and the lead obtained from them respectively be kept apart; for if the lead rich and poor in silver were melted together, unnecessary expense would be incurred in the subsequent desilverization.

According to Pattinson, in lead-works in the North of England the total quantity of coal consumed in the reduction of litharge,

inclusive of that used as reducing agent, was $3\frac{1}{2}$ cwts. per fodder of 21 cwts. of lead reduced, a large quantity for the present day. The cost of reduction per ton of litharge at lead-works where coal was delivered at 2*s.* 11*d.* per ton, is given by Mr. J. A. Phillips as 3*s.* 0·8*d.*, and by Richardson on the average, including pot-dross, as 3*s.* 5·9*d.* But as the price of labour, fuel, and materials differs much in different localities, and varies considerably from time to time even in the same locality, too much importance should not be attached to statements of cost of production.

Reduction in the Bleiberg Furnace.—This furnace seems well suited for the reduction of litharge by charcoal, and it is in use for that purpose at some continental lead-works. What has been stated concerning the third and last stage of the Bleiberg process is equally applicable to the reduction of litharge, so that the reader is referred to the description of that process in this volume.

At the Friedrichshütte, Tarnowitz (see p. 357), this kind of furnace is employed for the reduction of the skimmings or pot-dross obtained in Pattinsonization. The furnace is represented in the annexed woodcuts (figs. 140 to 143 inclusive).[1]

It will not be necessary to give a detailed description of it, as it is hoped the woodcuts will be sufficiently understood without. The interior of the furnace, wherever it is to be in contact with lead or its oxide, is made of heavy brasque,[2] carefully and solidly stamped down. By this means the brick-work is protected both from permeation by lead and from corrosion by oxidized compounds of lead. Owing to the low conductivity of the brasque for heat, fuel is economized to the maximum, not, one should think, a very important item in this process when the fuel is only coal-slack and can be had at a small price. In front is a cast-iron door suspended in the manner shown in fig. 143, which, when lowered, closes that end of the furnace. The bed slopes downwards, it will be perceived, from each side towards the median line, and from the fire-bridge to the front, where at the deepest point is a conical tap-hole in the brasque with the greatest diameter outwards. The tap-hole is made in the usual way by inserting a conical wooden plug during the preparation of the bed and stamping the brasque round it, after which the plug is withdrawn. When the furnace is in operation the tap-hole is stopped with clay, and is opened every 12 hours. The lead when tapped off runs into a

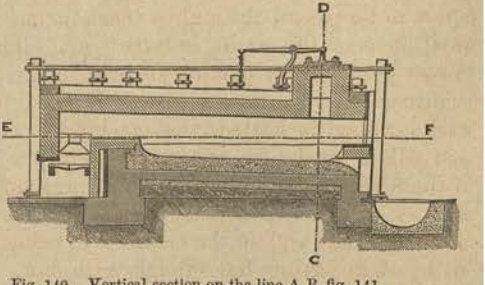

Fig. 140. Vertical section on the line A B, fig. 141.

[1] Copied from a plate illustrating Teichmann's paper in the Zeitschrift für das Berg- Hütten- und Salinenwesen im Preuss. Staate, 1867, vol. 15; and from the same source the descriptive details are derived.

[2] That is, coke-dust mixed with a considerable quantity of clay.

cavity or hearth underneath, which is lined with heavy brasque and the top of which is level with the smelting-house floor. The hearth is protected at its circumference by a cast-iron ring, and is kept covered with an iron plate, except during tapping. A cast-iron pot has been tried as a substitute for this hearth, but did not answer, because, firstly, in spite of preliminary heating it soon cracked [or rather because it was a bad one? —J. P.]; and, secondly, the lead after tapping became cold so quickly that it could hardly be skimmed. The gaseous products of the furnace ascend through a hole in the roof into a flue provided with a damper; and thence pass into a subterraneous culvert leading to a stack 150 feet high. The furnace is worked in 12-hour shifts, by one smelter, an assistant, and two labourers.

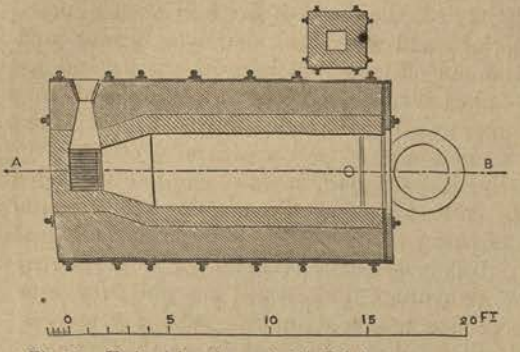

Fig. 141. Horizontal section on the line E F, fig. 140.

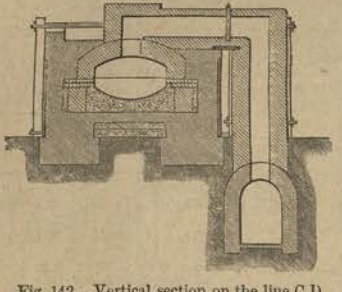
Fig. 142. Vertical section on the line C D, fig. 140.

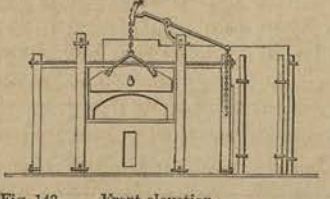
Fig. 143. Front elevation.

As the dross to be treated consists chiefly of oxide of lead, its reduction is a very simple operation.[3] The furnace, when the bed has been freshly made or repaired, is slowly dried and afterwards heated to strong redness. Sufficient dross, duly mixed with carbonaceous matter, is then introduced to cover the entire bed to the thickness of about 3″. The fire-place is charged with coal and the damper is so adjusted as to maintain the requisite temperature. The carbonaceous residue produced in poling in the desilverizing pots and cinders are then intermixed with the dross. In proportion as lead is reduced and collected at the lowest part of the bed, fresh dross and carbonaceous reducing matters are supplied from time to time. A charge of from 20 to 25 centners of dross is added at intervals of 3 or 4 hours. The slag which is formed and swims more or less

[3] After consultation with an experienced lead-smelter, I have ventured to make a few deviations from the German description, which, however, are of secondary importance.

completely molten on the surface of the lead must be well rabbled in order to remix the dross and carbonaceous matter. In 12 hours from 55 to 60 centners of lead are reduced. Before tapping, and after the slag has been strongly heated, the doors of the furnace are opened in order to cool the interior; and when the slag has become sufficiently solidified it is skimmed off, removed in iron trucks, and put aside for smelting in the blast-furnace. About 25 centners of dross are now thrown over the upper part of the bed towards the fire-bridge, after which from 55 to 60 centners of lead are tapped off into the receiving hearth, so that the bed always remains completely covered with lead to prevent the adhesion of slaggy matter which would otherwise occur. The lead being still more or less impure, small coal is thrown upon it, and it is poled with the use of a perforated skimming-ladle; and the skimmings thus formed are put back into the furnace. The litharge-slag produced in this reduction process is stated to be composed chiefly of metallic lead in small particles, and of sulphide, sulphate, and silicate of lead, and to contain iron, zinc, alumina, manganese, lime and magnesia.

In the following table are presented the results of the process at the Tarnowitz Works, during 1864 and 1865. It is in precisely the same form as given in the paper above referred to:—

Year.	Pot-dross treated.			Obtained.				
	1 Ctr. = 113·426 lbs. avoirdupois. Ctr.	Assay content.		Lead.		Reduction-slags.		
		Lead per cent.	Silver per cent.	Ctr.	Containing silver per cent.	Ctr.	Containing	
							Lead per cent.	Silver per cent.
1864	23,611	97·50	0·15420	19,438·50	0·1767	4232	73 20	0·0476
1865	30,716	97·40	0·16926	25,743·25	0·1883	5318	68·63	0·0652

Year.	100 ctr. of pot-dross yielded							Required.		Less than indicated by assay.	
	Lead.		Reduction-slags.			Total.		Coal slack. Ctr.	Brasque (1 tonne = 6 bushels English). To.	Lead. Ctr.	Silver. Pounds.
	Ctr.	Containing silver per cent.	Ctr.	Containing		Lead. Ctr.	Silver. pounds. (1 lb. = 7218 gr. English).				
				Lead per cent.	Silver per cent.						
1864	82·33	0·1767	17·92	73·20	0·0476	95·45	15·4007	5·59	0·10	2·05	0·0193
1865	83·31	0·1883	17·31	68·63	0·0652	95·69	16·9100	5·36	0·14	1·71	0·0160

COST OF REDUCTION OF POT-DROSS IN 1864 PER CENTNER OF LEAD OBTAINED.

	s.	d.
Labour	0	10·44
Fuel	0	2·36
Maintenance of furnaces	0	2·70
Smithy costs	0	0·58
	1	4·08

Reduction in the blast-furnace.[4]—At Freiberg a furnace similar in construction to that described at p. 309 is used for this purpose. It is, however, only 8′ high, from the hearth to the mouth. The bed is of brasque, and slopes downwards and forwards only 3″ from the twyer side or back. Coke is the fuel and no flux is required; but when the litharge is impure and impregnated it may be with marl from the bed of the German cupellation-furnace, 10% of old lead-slags are added. About 900 centners (between 40 and 50 tons) of litharge derived from the direct cupellation of ore-furnace lead are passed through the furnace in the course of 24 hours, with a consumption of about 10 bushels of coke (about 29½ bushels English), and a yield of about 90 centners of lead per 100 centners of litharge. During this period the furnace is tapped about 20 times and 8 men are employed. Of litharge from Pattinsonized lead[5] only about 500 centners can be reduced in 24 hours, with the labour of five men; and of impure residual litharge got out of the German cupellation-furnace after the completion of the process, only 300 centners can be treated in the same time. The litharge-slag, which is produced in this process, contains from 25% to 30% of lead. It is smelted with the addition of 3% of iron-pyrites in the same kind of blast-furnace as above mentioned; and about 100 centners are passed through in 24 hours. The products are slag, regulus, and very impure lead. The lead is softened in a reverberatory furnace and afterwards Pattinsonized. The regulus is worked up in lead-regulus smelting (see p. 316). The slags, which are black and vitreous, and contain on an average 5% of lead, are treated in the ore-furnace (?).[6] Samples prepared from large quantities of these slags have been analysed by Richter, whose results are as under:—

Composition of Litharge-Slags.

	I.	II.
Silica	36·66	52·00
Alumina	6·12	7·40
Lime	5·76	8·63
Magnesia	1·43	0·81
Protoxide of iron	30·42	25·11
Protoxide of lead (PbO)	8·38	3·10
Dioxide of copper (Cu^2O)	1·07	0·18
Sulphur	3·21	0·51
Intermixed coke	7·32	2·10
	100·37	99·84

Part of the sulphur was combined with calcium, but most of it was contained in the intermixed coke.

[4] Plattner's Vorlesungen, 2. 129. I have translated literally as far as I thought desirable.

[5] Pattinsonized lead *rich* in silver? Litharge from Pattinsonized lead *poor* in silver is as quickly reduced as that from ore-furnace lead. Certain impurities are concentrated along with the silver, and then the reduction of the litharge proceeds more slowly.

[6] There seems to be an error in the German description. The sentence is "Der Stein kommt zur Bleisteinarbeit, die Veränderungsschlacke aber zur Bleisteinarbeit."

I. From the Mulde Works. It is a mixture of tribasic and bibasic silicates.

II. From the Halsbrücke Works. It consists essentially of bibasic silicates.

At Clausthal litharge is reduced in a blast-furnace about 20′ high and not, as formerly, in a much lower furnace: and with this change of altitude, it is reported that the yield of lead is greater, the reduction campaign is prolonged, and less litharge-slag is formed. Kerl gives the following dimensions of the furnace :[7]

From the twyer to the mouth 15′ 9″, and to the lowest part of the hearth 3′ 3″. Height of the twyer above the top of the dam-plate in front 1′ 2″. Width (*i.e.* from side to side) of the fore-wall on a level with the top of the dam-plate 2′. From front to back, at the mouth 2′ 5″,—on a level with the twyer 3′ 2″,—and 5′ above the top of the dam-plate 2′ 4″. The twyer or back-wall slopes outwards 4½″ from the hearth-bottom to the height of 6′ 7″, above which it is perpendicular. The fore-wall slopes outwards 6″ from the surface of the brasque bed to the height of 6′ 10″. Diameter of the twyer, which is D shaped with the flat side downwards, 2½″.

English lead-smelters will probably smile at the precision with which these dimensions are stated, and rightly conclude that an inch or two more or less cannot be very important, seeing that the furnace in the course of working may soon become altered to more than that extent by corrosion within or distortion by heat. There is, however, one point in its construction which is interesting and a knowledge of which may be useful. It is the lining of the lower part of the furnace with what are designated "coke-stones." Instead of this material, bricks made of not very refractory clay (*Barnstein*) were formerly employed, which, owing to their highly siliceous nature, were powerfully corroded by oxide of lead; and as a consequence much slag was generated and a reduction campaign was shorter than with the recent furnace. The "coke-stones," or, as I will designate them, coke-bricks, are stated to have been invented by Kast, smelter at the Clausthal Works. They are thus made. The coke is used in the state of fine powder, obtained by pounding and sifting; and this powder is stirred and thoroughly mixed with clay and water until the mass becomes sufficiently plastic to admit of its being moulded into bricks in the usual manner. The bricks are only air-dried previously to use. The proportions of these ingredients (by weight) which suffice to make 28 bricks, 12″ long, 7″ wide, and 6″ thick, are as under[8]:—

Clay	199·3 pounds.
Coke-dust	313·1 ,,
Water	112·3 ,,
	624·7 ,,

[7] Die Oberharzer Hüttenprocesse, 2° ed. 1860. pp. 272, 277, 602. Kerl has given in this work excellent drawings of the furnace. See also Plattner's Vorlesungen, p. 126.

[8] I have not thought it worth while to reduce these weights into English.

The loss of weight in that quantity by air-drying amounts to 15 lbs. The clay at Clausthal has the following composition according to Bruns :—

COMPOSITION OF CLAY AT CLAUSTHAL.

Silica	77·89
Alumina	13·20
Sesquioxide of iron	5·27
Carbonate of lime	3·12
Carbonate of magnesia	1·33
	100·81

The furnace at the commencement of a campaign is supplied with charcoal, which is the fuel, litharge, and litharge-slags, in the proportions of 25, 174, and 20 pounds respectively, the latter in order to form the nose. The litharge broken into lumps is put in against the fore-wall and sides, and the slags against the back-wall. The object of this mode of filling is to keep as much charcoal as practicable between the twyer and the lead, as it trickles down in front; and so to prevent any reoxidation of the latter. Besides, the same condition would obviously be favourable to the reduction of any oxide of lead which might chance to descend in front of the twyer. Three men are employed. The indications of the furnace working well are a dark mouth (*i.e.* without flame), a dark eye (*i.e.* of the twyer), and a tough slag. In the treatment of 100 centners of litharge were consumed—

	Centners.
Charcoal	11·0
Litharge-slags	11·5

The products were—

	Centners.
Lead, containing 0·375 quint of silver per ctr. (about 1½ dwt.), and small quantities of copper, antimony, arsenic, iron, and zinc	88·0
Litharge-slags, containing from 8 to 10 lbs. of lead per ctr., thrown away	1·6
Ditto re-smelted in the same process	11 0
Skimmings (Bleidreck) of the reduced lead, containing 75 lbs. of lead per ctr.	2·4
Fume, containing 78 lbs. of lead per ctr.	0·4

The total cost of reducing 100 centners of litharge is reported as 2*l.* 2*s.* 2*d.*

In the Upper Harz smelting works the above-mentioned treatment is adopted, but only for the greenish-black, bright, dense and brittle litharge, formed in the German cupellation process, in the middle of the *Abstrich* period. The impure frothy *Abstrich* produced at the beginning and the yellow *Abstrich*, poor in antimony, produced at the end, are treated in Schlich or fine-ore smelting. Any metallic lead which may be separated is cupelled in the German fashion.[9] According to Streng, the specific gravity of Clausthal hard lead is 10·441 and that of Lautenthal is only 9·360. The ingredients in these leads are reported by the same authority to vary in proportion

[9] Op. ant. cit. p. 133.

as follow:—lead 77·36% to 88·84%,—antimony 8·16% to 22·75%,—copper 0% to 0·68%,—iron and zinc 0% to 0·48%.

In Freiberg, as previously stated, the *Abstrich* is treated precisely in the same manner as litharge, except that it is reduced in conjunction with some lead-slags.

Reduction in the German cupellation-furnace.—At Przibram 75 centners of impure black litharge (*Abstrich*) are melted down at a time, without blast, but with a strong fire, in a German cupellation-furnace, having a bottom of heavy brasque instead of marl. After about 20 hours the furnace is tapped and the molten mass within is made to flow into a cavity lined with brasque in the floor of the smelting-house. Any metallic lead which may have been intermixed with the litharge collects at the bottom of this cavity, while the slag, as it is termed, runs over the edge of it. The lead, which contains from 2 to 3 loths of silver per centner (*i.e.* about from 20 to 30 ozs. per ton), is cupelled by the German method. The slag contains from about 50% to 60% of lead, and yields on reduction hard lead (*Hartblei*), which contains from 18% to 24% of antimony.[1] The special object of this process is the separation of any metallic lead existing in the *Abstrich*. Moreover, this small quantity of lead will desilverize the *Abstrich*, and such a result may probably be a point in the process.

Chinese Method of Reducing Litharge.

I am indebted for the following account to my friend Mr. C. Tookey (1870).

The Chinese, like other Eastern nations, carry on their metallurgical processes on a small scale. A method of reducing litharge which would astonish English lead-smelters, came under my notice while in Hong Kong. The operation was conducted in a small shed with a square hole in the roof, which served the double purpose of admitting light, and allowing the escape of smoke and fume. On a hearth raised 6″ from the ground, a square furnace having an internal diameter of about 12″ had been built of ordinary Chinese bricks; there was no covering at the top, and as usual in China where much heat is required, a blowing-machine supplied a blast of air through a tube which terminated near the bottom of the furnace. The fuel was charcoal. The litharge, in pieces of the size of a cubic inch, was reduced in a large clay crucible; the crucible appeared to be about half full of the litharge, and when the temperature had been sufficiently raised the workman threw in fragments of roll-sulphur until enough lead had been produced to allow of its being laded by means of a small crucible into iron moulds capable of holding between 1 and 2 lbs. This reaction between litharge and sulphur was continued as long as the crucible lasted; the consumption of sulphur being much larger than necessary from the crude manner in which the process was conducted.[2] The workman informed me that the litharge came

[1] Plattner's Vorlesungen, p. 132.

[2] See p. 18 of this volume for an explanation of the theory of the process.

from California; it was not pure, and had probably been produced in some refining operation. I afterwards examined the lead, it was tolerably soft, and contained a little silver with a trace of gold.

The blowing-machines used in Hong Kong and Canton, are usually cylindrical, the principal of their construction being similar to that of which a drawing is given in Vol. II. of this work, page 746. I saw a large one at Kowloon, worked by two men for producing a blast of air in a lime-kiln, where for want of limestone they were burning brain coral.

REMARKS ON THE VARIETY OF LEAD-SMELTING PROCESSES, AND THE INFLUENCE OF DIFFERENT FOREIGN MATTERS IN THE ORE.

The reader cannot fail to have been struck with the variety of methods that have been adopted for the extraction of lead from its ores, and described in detail in the foregoing pages of this volume; and he will naturally enquire, whether good reasons can always be assigned for the fact; or, what is equivalent, whether any necessity exists for such variety. A question of this kind is certainly one of the most difficult that can be presented to the consideration of the metallurgist: it requires for its satisfactory solution a combination of practical and scientific knowledge rarely to be found in one individual,—a thorough acquaintance with local circumstances,—accurate knowledge of the nature of the ores in the state in which they are delivered to the smelter,—minute and trustworthy data respecting charges, yields, losses by volatilization or otherwise, and costs,—results which have been obtained by the exercise of equal manipulative skill, and under conditions which are indispensable for the comparison of one process with another,—and, lastly, what may be designated the necessities and capabilities of the case, such as the quantity of ore and regularity of its supply, the capital at the command of the smelter, &c. It is curious to note the dogmatism which has been displayed by some metallurgical writers in dealing with this question, how readily and confidently they have arrived at conclusions, and how often those conclusions have been proved erroneous.

By way of illustration, let us take a very simple case, and suppose the question to arise, whether the Reverberatory furnace or the Ore-hearth should be selected for smelting galena of such a quality as long experience has shewn to be equally suitable for both. Let the reader imagine himself in the position of a smelter called upon to answer that question, and he will perhaps be astonished to find how many other questions will immediately crowd upon him, which must be considered before he can arrive at a satisfactory decision. The first point to be settled is obviously, which will yield the greatest return for capital invested? But how is this point to be ascertained, since smelters of great experience are not themselves unanimous about it, and there are smelting-works in the North of England where both kinds of furnace are used? According to Gruner, "It is evident that the Ore-hearth ought everywhere to give way to the method by

reaction" (*i. e.* the air-reduction process);[1] and the reasons which he assigns for this statement are, that in the comparative trials made in Carinthia with the same kind of galena in the Bleiberg furnace and the modified American Ore-hearth, the loss of lead by volatilization in the latter was much greater than in the former;[2] and that, notwithstanding the Ore-hearth used in those trials was placed under an exhausting hood for carrying off the smoke, the work was found to be fatiguing and dangerous. Now, greater loss of lead does not necessarily imply less pecuniary return, and this in all manufacturing operations is the main point. With regard to insalubrity, it must be shewn to be impracticable to apply efficient means of ventilation in the case of the Ore-hearth, before pronouncing sentence of condemnation upon it, which has assuredly not been done; and as to fatigue, smelting in the Ore-hearth is not more laborious than many other metallurgical processes, even some of those connected with lead. From what has just been advanced, it will probably be admitted that the justice of the verdict of Gruner upon the Ore-hearth is, to say the least, not so evident as he declares; and in some localities where peat is cheap and coal dear, this efficient, though somewhat primitive, little furnace may be expected to hold its own against the Reverberatory furnace. Yet Gruner is right in asserting that in the case of such a metal as lead, which is worth nearly 20*l.* a ton, diminution of the loss of the metal in smelting is the chief consideration, to which the consumption of fuel is nearly always subordinate.

In a former part of this volume (p. 284), statements have been presented concerning the cost of smelting the same kind of ore in each of the furnaces in question in a particular locality, and the result was stated to be in favour of the Ore-hearth; but coal, it should be remembered, was dear in that locality and peat sufficiently cheap. On the other hand, it is asserted by a practical smelter, in whose accuracy and experience I have great confidence, that such ore might be smelted in the Reverberatory furnace in other localities, where coal is cheap, for considerably less than the sum reported to have been expended in smelting it in the Ore-hearth. The object, however, of these remarks is not to enquire exhaustively concerning the relative advantages of the two methods of smelting, but to shew how difficult

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[1] Ann. des Mines, 6 ser. 1868, 13, pp. 331 and 375. The principle of the reduction of galena in the Ore-hearth is essentially the same as that of the so-called method by reaction, or, as I have designated it, the Air-reduction process. The only difference is that in the former reduction immediately follows oxidation, the two practically occurring *pari passu*; while in the latter a considerable interval elapses between them. Gruner, however, asserts that in the Ore-hearth the sulphur of the galena alone burns, leaving the lead in the metallic state; and, in illustration, he cites the reduction of a fragment of galena on charcoal before the "semi-oxidizing" flame of the blow-pipe. There is no proof whatever that such is the case; and it is hardly conceivable that, under the circumstances of temperature and excess of oxygen, the lead should not also simultaneously undergo oxidation. But any oxide so formed would instantly act on the subjacent sulphide, and cause the separation of metallic lead.

[2] Yet Gruner asserts, in another part of his memoir (p. 342), that the Ore-hearth succeeded at Przibram, and was only abandoned there on account of its insalubrity.

it is to arrive at a positive conclusion on such an apparently simple subject, notwithstanding the long period during which each has been in constant operation, in some instances in the same district and even in the same establishment. If this be so, it will obviously be much more difficult to decide as to the relative advantages of many of the various processes applied to the treatment of galeniferous ores, differing notably from each other in the nature and proportion of the associated foreign matter.

Of all the elements, which relate to the choice of methods of lead-smelting, probably the most influential are the nature and proportion of the foreign matter in the ore, and the nature and cost of fuel. Where coal is cheap and suitable, it may be affirmed that there is no ore which, supposing it to contain sufficient lead to admit of its being profitably smelted at all, cannot be treated in the Reverberatory furnace; and in England, where that condition exists, the most impure as well as the purest ore, as we have seen, is smelted with advantage in such furnaces. The same may also be averred with respect to smelting in localities where wood or other vegetable fuel abounds; and, as in Sweden furnaces have been successfully constructed on the reverberatory principle for burning peat, and employed in the manufacture of iron, it is reasonable to suppose that this fuel might also be advantageously applied to the smelting of lead in similar furnaces somewhat modified. On the other hand, Blast-furnaces are extensively and profitably used for lead-smelting on the Continent, with charcoal or coke as the fuel, especially for poor and impure ores. However, the Reverberatory furnace has in recent years, owing to the development of coal-fields, been introduced into various Continental lead-works, but not to the exclusion of the Blast-furnace in which certain descriptions of ore continue to be treated. Yet it has made its way very slowly; and it was not until 1862, that it was adopted in Prussia at the Royal Lead-Works at Tarnowitz, notwithstanding the Prussian metallurgists must long previously have had ample opportunities of becoming acquainted with its merits in England.

With regard to the influence of the nature and proportion of foreign matter in the ore, much experience has been obtained, and much has been somewhat authoritatively asserted rather than clearly demonstrated. When the proportion of such matter is small, or what is equivalent, when the ore is rich, containing, say, 80% of lead or more, its effect, whatever may be its nature, is not very material. Information concerning the nature of the various kinds of foreign matter occurring in lead-ores has been given in the preceding pages of this volume, and attention has been particularly directed to the inconveniences which it may occasion in the various processes of smelting. But on this subject the following additional remarks may be useful.

Iron-pyrites.—The presence of this sulphide increases the proportion of sulphate of lead formed by calcination (see p. 47), and appears to favour the oxidation of galena. In the first stage or preliminary

calcination, oxidation of the sulphur is only partial, so that in the second or melting-down stage, any sulphide of iron (the bisulphide of iron remaining unoxidized, having, it may be assumed, been reduced to sulphide) would be diffused through the mass, and contact between the oxidized products and unchanged sulphide of lead would be, consequently, less extensive, and, *pro tanto*, reduction retarded. But regulus of iron and lead would be formed, and the sulphide of lead in such a regulus would not be so accessible to the reducing action of the oxidized products of lead as the same sulphide when isolated. Moreover, the oxygen of those products would be largely consumed in the oxidation of sulphide of iron, with separation of metallic lead; and, if this be so, it is manifest that, in the absence of sulphide of iron, more lead would be reduced in a given time than in its presence. The ultimate products of the oxidation of bisulphide of iron during calcination are protoxide and sesquioxide of the metal and perhaps some basic sulphate of sesquioxide; but what may be the relative proportions, under the circumstances, I am unable to state. Iron-scales, which contain a less proportion of sesquioxide than magnetic-oxide, exert, according to Berthier, no action when heated with galena; but when the latter is heated with sesquioxide of iron, sulphurous acid is evolved, with corresponding, yet only partial, reduction of that oxide to protoxide: in which case metallic lead must be set free, though it may be immediately afterwards oxidized at the expense of another portion of the sesquioxide of iron present. Hence, under these conditions, actual separation of metallic lead may not occur. When perfectly liquid slag is produced, and silica is present in sufficient quantity to form fusible silicate of protoxide of iron, the whole of the iron will be found in the slag in that state of combination, sesquioxide of iron being reduced at a high temperature by contact with silica to protoxide. But when only pasty slag is formed, or sufficient silica is not present, this oxide may exist mechanically diffused through the slag. The presence of iron-pyrites in notable quantity gives trouble in smelting in the Flintshire furnace by causing the formation of regulus; the charge becomes pasty, and runs down into the tap-hole cavity, or, as the smelters say, "it will not stand fire;" and, as a consequence, the work does not progress in a satisfactory manner.

Copper-pyrites.—In the melting-down stage in the Flintshire furnace, the same reaction would occur as in the case of iron-pyrites; and in addition, there would be reactions between the oxide of copper formed during the first stage or calcination and the unchanged sulphide of lead, and between the oxidized products of the lead and the unchanged disulphide of copper. Regulus of iron, copper, and lead would be formed, and the reduced lead would be cupriferous. These reactions are somewhat complicated, exclusive of those relating to the sulphide of iron in the copper-pyrites; for protoxide, sulphate and sulphide of lead, and disulphide and dioxide of copper, possibly also some protoxide and sulphate of copper, are concerned. When protoxide of copper (CuO) is treated with sulphide of lead in certain proportions, sulphurous acid

is evolved, copper is separated both in the metallic state and in that of regulus of copper and lead, and slag consisting of dioxide of copper (Cu^2O) and protoxide of lead is formed.[3] But when the proportion of protoxide of copper is relatively large, as in a mixture prepared according to the formula $PbS+3CuO$, no regulus is produced, but only brown-red slag and nearly pure copper, to the extent of about $\frac{1}{6}$ of the total copper. In these cases the action is not simple, for a secondary reaction will take place between the reduced copper and sulphide of lead. The effect of dioxide of copper (Cu^2O) would probably be similar to that of protoxide, but I cannot advance experimental proof on this point. The evils which may result from the presence of a notable quantity of copper-pyrites in galeniferous ore are the formation of cupriferous regulus, necessitating after-treatment, and the production of lead contaminated with copper. With regard to the action of the sulphide of iron in the copper-pyrites, what has been stated on the subject of iron-pyrites is equally applicable to both cases.

Sulphide of zinc.—According to Kerl, the presence of zinc-blende favours calcination, by acting as a stiffening ingredient (Ansteifungsmittel), so keeping the mass open, thereby facilitating access of air, and enabling the charge to "stand fire."[4] Both elements of any of this sulphide remaining unchanged after calcination would be oxidized in the second or melting-down stage by contact with the oxidized products of lead, with the formation of sulphurous acid and oxide of zinc, and separation of metallic lead. Some of the oxide of zinc in the calcined ore would be reduced in the Blast-furnace; and it is asserted that the escaping vapour of the metal would greatly promote the volatilization both of lead and silver. Any of this oxide which might escape reduction would enter the slag, and tend to render it less fusible. Unchanged sulphide of zinc would in part pass into the regulus, if regulus be formed, and in part remain entangled in the slag, rendering both more refractory; but by contact with metallic iron the sulphide would be decomposed, zinc being set free and sulphide of iron generated. The difficulties caused by the presence of a large quantity of zinc-blende in lead-smelting have been already exemplified in the descriptions given in this volume of various processes, especially that of Przibram; and, it would seem, that hitherto they have proved insurmountable. The evil of a too refractory slag from the presence of silicate of zinc or intermingled sulphide of zinc may be counteracted by the addition of fusible slag, which, of course, implies increased consumption of fuel and prolongation of the process of smelting. Rivot asserts that "blende is partially decomposed in the upper part of the Blast-furnace by the action of the vapour of water."[5] But, it may be asked, whence comes this vapour of water? It might be supposed that the moisture in

[3] See Vol. I. of this work, p. 254, where the results of experiments on this subject are reported.

[4] Handb. d. metallurgischen Hüttenkunde, 1863, 2. p. 242.

[5] Principes Généraux, 1860, p. 105.

the air, which is blown into the lower part of the furnace, would be quickly and wholly decomposed in its ascent through a column of highly incandescent carbonaceous matter; and that any moisture in the solid materials introduced into the furnace would be expelled and escape upwards, before descending to that zone, where the temperature would suffice to cause the reaction between it and sulphide of zinc. With respect to the Iron-reduction process, Gruner states that if sulphide of zinc should descend to the region of the twyers, and there come in contact with metallic iron, it would be attacked by the latter; and the resulting vapour of zinc would be again sulphurized or oxidized in the upper part of the furnace by galena or carbonic acid, and so enter upon an endless circuit, except that which might escape oxidation, and which would be evolved from the mouth of the furnace.[6] But is it certain that such oxidation would take place where any carbonic acid that might occur would necessarily be associated with a large quantity of carbonic oxide? Gruner maintains that the so-called Method of Reaction is preferable to the Iron-reduction process, when galena mixed with blende is smelted, because in the former the zinc in vapour would carry off lead, while in the latter the whole of the blende would be oxidized and the resulting oxide of zinc would pass into the slag. He concludes that the Iron-reduction process is "rarely advantageous, even when oxidized ferruginous matters are employed as the source of the iron; that it is neither suitable for argentiferous galenas, pure galenas, nor blendic galenas; that the only case in which its use seems rational is that of quartzose or coppery galena, which is but slightly argentiferous; and that even then, when the ore is mixed with pyrites, it is better to adopt the method of calcining and reduction by deoxidation."

Sulphide of antimony.—The facts to be borne in mind with reference to this subject are, first, that metallic lead is not separated when antimony is heated with sulphide of lead, a kind of antimonio-sulphide of lead appearing to be formed, from which it may be reasonably inferred, that sulphide of antimony is not reduced when heated with metallic lead; and, secondly, that sulphide of antimony is oxidized when heated with protoxide of lead, a fusible product consisting of oxide of antimony and lead being produced, and metallic (antimonial?) lead separated. But further investigation is needed to settle definitely the precise reactions which occur in these cases. However, the lead, which results from smelting antimonial galena in the Reverberatory furnace, contains antimony; but the product of the oxidation of sulphide of antimony, formed during calcination, passes, at least for the most part, into the slag; hence hard or antimonial lead is obtained in smelting such slag. What action takes place when sulphide of lead is heated with oxide of antimony or antimonious acid, or when sulphide of antimony is heated with sulphate of lead, I do not certainly know. In the Blast-furnace, any sulphide of antimony which may be present, and come in contact with metallic iron,

[6] Ann. d. Mines, 1868, 6. ser. 13, p. 357.

resulting from the reduction of oxide of iron, will be decomposed with the formation of sulphide of iron and separation of metallic antimony, of which part will be volatilized, with increase, it is said, of the loss of silver and lead by volatilization, while the rest will pass wholly into the lead, except in certain cases when speise is produced, when some may also pass into that substance.[7]

Arsenic.—This element may be present in iron-pyrites or certain other sulphides, in which case some of it will be volatilized during calcination, but part will remain in any of the original sulphide left unoxidized, and part in the oxidized products in the state of basic arseniate. In the succeeding or reducing stage of the smelting process, the arsenic not removed by calcination will in part be volatilized, and in part pass into the reduced lead. Every arseniate, of which the base is capable of combining with silica at a high temperature, is wholly decomposed when strongly heated in contact with that substance, the arsenic acid being resolved into oxygen and arsenious acid. The contamination of the lead with arsenic, under the circumstances, is accounted for by the fact that metallic arsenic is separated when arsenious acid or sulphide of arsenic is brought in contact with strongly heated lead (see pp. 62 and 71). It is asserted that the presence of arsenic in lead-ores increases the loss both of lead and silver from volatilization during the process of smelting.[8] In the Blast-furnace, in which metallic iron may be set free by the reducing action of the incandescent fuel and furnace gases upon oxide of iron, or may have been originally added, the presence of arsenic may give rise to the formation of a speise or arsenide of iron; but arsenic is not to be regarded as an evil if nickel or cobalt be present, because a speise of those metals will then be formed, from which they may be profitably extracted.

Sulphide of silver.—The effect of calcination with access of air upon this sulphide, both when isolated and in the presence of other sulphides, will be fully described hereafter. It suffices now to state, that when either it or any complex argentiferous sulphide is heated with metallic lead, the whole of the silver passes into the lead.[9] When metallic iron is present in the material smelted,—having either been added to the charge, or reduced from oxide of iron during the process, and lead-regulus is generated, it is found that, owing to the affinity of sulphide of silver for sulphide of iron, when the regulus is poor in lead and rich in iron, it contains proportionally more silver. Hence, as the quantity of silver in argentiferous lead-regulus will in a certain degree be proportionate to that of the iron contained in that product, and as the desilverization of such regulus must be effected through the agency of lead, it is considered desirable to prevent the formation of highly ferriferous regulus, by reducing the quantity of iron added to the charge, or if no such addition is made, of altering

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[7] Kerl, Handbuch, 1863, 2. p. 121.
[8] Ibid. p. 45.
[9] That is, assuming metallic lead to be separated, which, as previously stated, would not occur in the case of sulphide of antimony.

the composition of the smelting-mixture so as to lessen the reduction of iron in the furnace.[10] Experience has shewn that in desilverizing regulus by fusion with lead, it is necessary to vary the quantity of lead used according not only to the proportion of iron, but also to that of the copper when this metal is present; the less the quantity of lead in the regulus, the greater will be that of metallic lead required to be used for that purpose.[11] Temperature also is stated to be not without influence on desilverization by this means.

Silica.—Kerl asserts that silica, when present in galeniferous ore, only to the extent of $\frac{1}{4}$% or $\frac{1}{2}$%, exerts an injurious influence, by producing even at the beginning of the calcination an easily-fusible slag, which coats the product like a varnish, and makes it difficult to attain the requisite degree of oxidation; that 5% or 6% of silica suffices completely to hinder the reactions (die Reactionen schon vollständig gestört); and that the more intimately it is mixed the more powerful will be its action in that respect.[1] In support of this assertion he cites the results of experiments conducted at Poullaouen and in the Upper Harz. Now, if the presence of 5% or 6% of silica entirely check calcination, how, it may be asked, could the galena in the ores of Commern, which contain a much larger proportion of silica, be converted by calcination into silicate of lead? (See p. 356 of this volume.) Although silica in notable quantity may tend greatly to impede calcination, yet it is exaggeration to affirm that it wholly stops it. Neither is it true, as has been maintained, that galeniferous ores rich in silica cannot be smelted in the Reverberatory furnace. In any case these ores must be first well calcined, when the galena will be thereby transformed for the most part into silicate of lead; and grey-slag, in which the lead exists mainly in the state of silicate, is continually the subject of reduction in such furnaces in England (*e.g.* the Flowing-furnace). Whether it may not be more profitable to treat highly siliceous galena by calcination and subsequent reduction in the Blast-furnace is another and widely different question.

Carbonate of lime.—This substance is frequently present in lead-ores as dressed for smelting in sufficient quantity materially to stiffen the charge, and may therefore be advantageous in the smelting of certain ores. It is converted into lime during calcination, and some sulphate of lime is also formed. So far as concerns calcination, it may practically be regarded as chemically inert matter; and in the "setting-up" stage in smelting in the Flintshire furnace when lime is added in considerable quantity, its action, as we have seen, appears to be mainly mechanical. When liquid slag is produced, as in the Flowing-furnace and Blast-furnace, lime serves to displace oxide of lead from silicate of lead, and so to facilitate the reduction of the lead. According to Kerl, when the proportion of carbonate of lime exceeds 12%, this substance may from its mechanical action prove injurious;[2] but, I apprehend that it is not possible to assign such a precise limit

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[10] Kerl, Handbuch, 1863, 2. p. 125.
[1] Handbuch, 1863, 2. p. 41.
[11] Markus, B. u. h. Zeit. 1857, p. 68.
[2] Ibid. p. 44.

for all circumstances, because much will depend upon the nature and proportion of the other foreign ingredients of the ore.

Dolomite.—The observations which have been presented with respect to carbonate of lime will apply nearly equally to dolomite.

Carbonate of iron.[3]—When this substance is heated to redness both carbonic oxide and carbonic acid are evolved, and the residue consists of protoxide and sesquioxide of iron, in the ratio of $4FeO : Fe^2O^3$; but during calcination, much of this protoxide may be converted into sesquioxide by atmospheric oxygen. According to Kerl, experiments, made at Clausthal on the smelting of galena in the Reverberatory furnace, have shown, that spathic iron-ore in the presence of silica may act injuriously, by giving rise to the formation of easily-fusible silicate of iron; but when not present in too large proportion, it may be beneficial in the subsequent reactions, rather than hurtful.[4] The action of tribasic silicate of protoxide of iron upon galena has been previously described in this volume (p. 58). Kerl alleges that in smelting in the Reverberatory furnace, the presence of sesquioxide of iron necessitates more frequent repetition of what he designates the "roast-reduction processes," by which it may be presumed is meant "setting-up;" that as a consequence of such repetition, slag is produced containing less of the imaginary oxysulphide of lead, and consisting mostly of oxide and sulphate of lead; and that sesquioxide of iron, when present in large quantity, hinders the reactions in the melting-down stage by lessening the contact between the constituents of the mass.[5] In the Blast-furnace, carbonate of iron will be reduced to a greater or less extent, and the resulting metallic iron may then act as a desulphurizing substance; and with a view to this action, a certain proportion of it may be designedly left in the ore in the operations of dressing.

Fluor-spar.—This substance, which is often associated with galena, may be regarded as chemically inert, except when sulphate of baryta is also present; in which case it may serve as a flux to the latter when in smelting it is desired to produce liquid slag. It should likewise be borne in mind that it forms readily fusible compounds with sulphate of lead, which while molten are very liquid. In smelting products containing fluorine and sulphate of lead, such as Derbyshire lead-slags (see p. 241) fluorine is disengaged, as is shewn by the corrosion of the glass of windows in houses surrounding works in Birmingham, where such slags are treated in reverberatory furnaces. The sulphuric acid which is evolved under those circumstances from the sulphate of lead, acts upon the fluoride of calcium in the slags and disengages fluorine in some state of combination or other in which it is capable of attacking glass.

Sulphate of baryta.—This substance is a not uncommon constituent of British lead-ores; and on account of its high specific gravity the dressing of ores containing it must not be carried too far, lest

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[3] See Vol. II. of this work, p. 142.

[4] Handbuch, 1863, 2. p. 42.

[5] Ibid. p. 45.

notable loss of galena should occur. In smelting barytic ores in the Reverberatory furnace, liquid slag may be readily obtained by the addition of fluor-spar, which is found occasionally in such ores. Sulphate of baryta is decomposed at a high temperature by silica with the formation of silicate which is fusible.[6] As sulphate of baryta is reduced to sulphide of barium by carbonaceous matter at a comparatively low temperature (see note at p. 334), it would undergo the like change in the Blast-furnace, and the resulting sulphide might, it is conceived, act in the following ways: it might become a constituent of any accompanying regulus; reaction might take place between it and silicate of lead—thus $2PbO,SiO^2+BaS=2BaO,SiO^2+2PbS$,—followed by the usual reaction between the sulphide of lead so formed and any oxide, sulphate, or silicate of lead, with which it might come in contact; possibly also, $BaO,SO^3+2PbS=BaS+2SO^2+Pb^2$—but this, let it be remembered, is only conjectural; and by contact with metallic iron, a regulus containing barium and iron might be produced. I have described such a regulus, which was formed in smelting iron-ores impregnated with sulphate of baryta in a large Blast-furnace (see the volume of this work on Iron and Steel, p. 895); it contained 43·91% of iron and 16·36% of barium, with small quantities of calcium, magnesium, potassium, sodium, manganese, and copper, and I was informed that it occurred between the slag and the pig-iron.

Clay and other silicates.—The term clay is far from definite in meaning, as it is applied to substances differing much from each other in composition and other respects. All clay usually contains free silica, and that will act in the manner already considered; but what would be the precise effect of a silicate of alumina unmixed with free silica, I cannot positively assert, though from the following statement of Berthier, it seems probable that protoxide of lead would enter into combination with both constituents of that substance, forming silicate and aluminate of lead, respectively: in which case its influence in the smelting of galeniferous ore would be practically similar to that of free silica. Berthier's statement is that a mixture of 1 part by weight of washed china-clay or kaolin and 5 parts of litharge is fusible, and the product is compact, free from bubbles, conchoidal in fracture, shining, transparent, and olive-green.[7] Galena may be associated with other silicates, as at Sala (see p. 296), with which the protoxide of lead, resulting from its oxidation in the process of calcining, may tend in a certain degree to combine; but I am not aware, whether such silicates have been found in dressed ore in sufficient quantity to produce any decidedly injurious effect on the operation of smelting either in the Reverberatory or Blast-furnace.

There are some considerations, which apply generally to all kinds of foreign matters in lead-ores, and which are so obvious as only to need mention in order to be properly appreciated, namely, the larger

[6] According to Berthier it required to be mixed with 7 or 8 times its weight of litharge to yield a fusible product. Tr. d. Ess. 1. p. 512. [7] Ibid. p. 511.

the proportion of such matters, the greater will be that of the slag produced, and, consequently, *cæteris paribus*, the quantity of fuel consumed. Moreover, as all lead-slags, even the cleanest, contain a sensible amount of lead, the loss of this metal in smelting will in some degree be proportional to the quantity of slag; and the more refractory the slag, the higher will be the temperature required for its fusion, the greater the loss of lead from volatilization, and the larger the consumption of fuel.

With regard to kinds of furnaces and their dimensions, relative as well as absolute, even the most experienced metallurgist may well hesitate to attempt generalization, in the face of such a vast accumulation of conflicting and bewildering accounts as have been published on the subject. But some metallurgical writers seem to entertain a different opinion, and have expressed themselves with great confidence not only as to the methods which it is best, that is, most profitable, to adopt in the treatment of particular ores, but as to the forms and dimensions of furnaces. Rivot writes concerning the influence of sulphide of antimony, "when the proportion of antimony is somewhat large, blast-furnaces ought to be employed, notwithstanding the treatment presents very great difficulties; it is impossible to apply the method of reactions to the reverberatory furnace. This method can only be employed for galenas which contain very little sulphide of antimony."[8] Now, I think I may venture to assert, that experienced British lead-smelters would not be deterred by this authoritative statement from treating such ores in the Flowing-furnace; and, provided they could be purchased at a reasonable price, would contrive to conduct the operation with advantage to themselves (see p. 260). It is certain that galena, impregnated with not a small quantity of antimony, has been and is profitably smelted in England in that kind of reverberatory furnace. It might be imagined, that as the action of the Blast-furnace is essentially deoxidizing and that of the Reverberatory furnace oxidizing, oxidized ores should be exclusively treated in the former; but may not grey-slag be virtually regarded as oxidized ore, and is it not daily smelted in some localities in England with profit in the latter? In some works where blast-furnaces had been erected at considerable expense for the treatment of that slag, they have been abandoned, especially on account of the great loss from volatilization, and reverberatory furnaces have been substituted for them.

The problem of the choice of method and furnace in lead-smelting is so complicated, and, as has been previously pointed out, necessarily involves the consideration of such numerous contingencies, that, at present at least, its solution is hopeless, and no precise and trustworthy rules can be laid down for general guidance. A method that may be best for one locality may be worst for another. There is a point to which allusion has not been made, and that is the force of tradition and habit. All men are liable to be affected, though

[8] Principes Généraux, p. 55.

unconsciously, by such influences; and no persons more so than those who have been trained from youth in the practice of any one manufacturing process, and eventually become the managers of works. Managers of equal experience and skill in the same kind of manufacture have been known to contend earnestly for the superiority of their respective methods of procedure; and as these are the men who have the amplest opportunities of observation, it is not surprising that discordance should prevail on matters like those in question. These remarks are not made with any view of disparaging the opinions of practical men, who, although they may in many cases —far fewer now than formerly—be ignorant of the science of the metallurgic art which they practise or direct, yet have acquired by long experience and observation that skill and, what I may term, eye-knowledge, which are essential to success, and without which they would fail, even supposing them eminently scientific. Let it not, however, be inferred from what I have just stated, that I undervalue the application of scientific knowledge to manufacturing operations.

Apart from the question of consumption of fuel, and the interference which may result from the oxidizing nature of the gaseous current flowing through the Reverberatory furnace, this apparatus is much more satisfactory than the Blast-furnace for the treatment of ores, like those of lead, in which complex chemical reactions occur. The contact between the constituents of the ore, which is essential to the completion of these reactions, may be prolonged indefinitely, the temperature may be controlled and rendered pretty uniform throughout, and perfect intermixture secured by rabbling. This is not so in the Blast-furnace, in which as soon as any portion of the substance operated upon becomes liquid, it trickles into the hearth, when it may be regarded as virtually withdrawn from further chemical action.

In the memoir on the Present State of the Metallurgy of Lead, which Gruner, Professor of Metallurgy at the School of Mines in Paris, has recently published, I find at the commencement the following passage:[9]—"I should wish above all, in this study, to render manifest the advantages and inconveniences of the methods pursued, to show how, in each given case, the most rational mode of treatment may be fixed *à priori*, without neglecting, as far as possible, any of the elements of the question to be studied." I regret that my information on the subject is neither sufficiently comprehensive nor trustworthy to enable me to perform the same task; but as the reader may desire to know what the general conclusions are at which Gruner has arrived on the subject of lead-smelting, I give the following literal translation of them.

1. The *ore-hearth process* ought everywhere to give place to the *method by roasting and reaction* (air-reduction process).

2. Rich, pure, non-quartzose ores ought always to be treated by

[9] Ann. d. Mines, 1868, 6. ser. 13. p. 325.

this latter method. The operation ought to take place in large reverberatory furnaces, with easy access of air, provided with a single fire-place and a receiving-basin, internal or external, placed in the least heated region of the furnace. The operation ought always to be conducted slowly, and to consist of two phases very distinct, *roasting* and *reaction* (*i.e.* mutually reducing action). For roasting, the layer of ore (Schlich) must never exceed from 3·15″ to 3·54″ in thickness. Roasting is to be effected at a low temperature, and ought to proceed as far as the theoretical limit of one equivalent of sulphate, or two equivalents of oxide, for each equivalent of sulphide. After the first firing, which produces lead, and fresh roastings and firings twice or thrice repeated, the rich residues (grey-slags) must be withdrawn from the reverberatory furnace, without having recourse to *ressuage* (*i.e.* reduction of those residues in the same furnace immediately afterwards, as in the Cornish and Bleiberg processes), but rather by practising this *ressuage* in a blast-furnace.

3. When the ores are impure or quartzose, the method by *roasting* and *reduction* ought, as much as possible, to be adopted. Limestone or oxidized ferruginous matters should be added as fluxes. The formation of regulus should be avoided by roasting well, at least when the ores are argentiferous without being cupriferous. The reduction-furnace should be narrow at the level of the twyers, circular in section, having two or several water-twyers, and provided, at this level, with cast-iron sides, cooled externally. The shaft ought to be wider from that level to the mouth. The furnace is to be worked with closed top, and the gases withdrawn through a side opening. When galena is mixed with blende, the latter must be separated, as far as practicable, by dressing; and what remains should be roasted with much care, in order that the zinc may pass into the slags in the form of oxide. Reduction of the oxide of zinc should be prevented by quick driving of the furnace and adding to the materials of the charge oxidized ferruginous substances without ever going beyond certain limits, otherwise the oxide of zinc will be reduced by the iron itself.

4. The *method of precipitation* (iron-reduction process) should only be adopted where fuel is deficient for roasting in the reverberatory furnace, or when the ores are plumbo-cupriferous. And even in this latter case, it is proper to roast them partially in order to reduce the weight of the regulus. Moreover, the furnace ought always to be prepared as for a reduction-smelting, especially when the iron is charged in the state of oxide, as it is suitable it should be.

After what has been previously advanced in this volume, it is not necessary to enter upon any special examination of these conclusions of Gruner. In some particulars they appear to me to be opposed to the results of long and varied experience; and I venture to assert that they will not command the unqualified acceptance of practised and intelligent lead-smelters.

Composition of different kinds of Foreign Lead.

Locality.	Specific gravity.	Copper.	Antimony.	Iron.	Zinc.	Silver.	Bismuth.	Sulphur.	Lead estimated by difference.
Soft Lead ... Przibram	11·357	0·083	slight trace	slight trace	..	0·014	..	slight trace	99·903
Soft Lead ... Joachimsthal	11·322	0·078	0·096	trace †	..	0·047	0·240	slight trace	99·539
Soft Lead ... Nagybánya	11·329	0·082	trace	..	..	0·036	..	trace	99·882
Soft Lead ... Schemnitz	11·343	0·055	0·285	..	..	0·002	..	..	99·658
Soft Lead ... Kremnitz	11·362 rolled; 11·319 re-melted	0·072	0·205	..	..	0·002	..	..	99·721
Soft Lead ... Neusohl	11·332	0·075	0·017	..	..	0·007	..	trace	99·901
Soft Lead ... Neusohl	..	0·090	0·166	trace	slight trace	not determined	..	..	99·744
Hard Lead	..	0·157	0·554	trace	..	not determined	..	..	99·289
Analysed by Von Lill.*									
Lead from revived litharge. Clausthal, Oct. 1861. Analysed by Streng	..	0·057	0·099	0·097	trace	..	..	..	99·837
Lead revived from litharge by coke. Clausthal, 1863. Analysed by Dr. Hahn	..	0·072	0·168	0·001	trace	..	..	..	99·759
Lead revived from litharge by charcoal. Clausthal. Analysed by Dr. Hahn...	..	0·067	0·046	0·001	trace	..	..	..	99·886
Lead from Altenau, by revival of litharge from enriched lead in Pattinson's process, and repeatedly Pattinsonizing revived lead. Analysis by Dr. Hahn...	..	0·026	0·022	0·015	0·006	..	..	..	99·931
Lead from regulus. Clausthal. Analysed by Lehzen	..	0·027	0·138	0·020	0·011	..	..	..	99·787
Pattinsonized lead. Lautenthal. Analysed by Streng	..	0·00096	none	0·00300	0·00420	..	..	..	99·99184

* The analyses were made in the Laboratory of the Imperial Assay-office, Vienna. Extracted from the Berg- und hüttenmännisches Jahrbuch, 1867, vol. 16, p. 264.

† With trace of nickel.

COMPOSITION OF DIFFERENT KINDS OF FOREIGN AND ENGLISH LEAD, ACCORDING TO ANALYSES MADE IN THE ROYAL LABORATORY AT CLAUSTHAL.

The quantity operated upon in each analysis was 100 grammes.		Copper.	Antimony.	Iron.	Zinc.	Silver.	Lead.
REFINED HARZ LEAD.							
Desilverized by Pattinson's process	Clausthal	0·03960	0·00250	0·00510	0·00100	0·00234	99·94946
	Lautenthal	0·03740	0·00160	0·00440	..	0·00193	99·95627
	Altenau...	0·03870	0·00130	0·00460	..	0·00230	99·95440
Desilverized by zinc.	Clausthal	0·00710	0·00250	0·00110	0·00080	0·00130	99·98720
	Lautenthal	0·00510	00·0340	0·00130	0·00120	0·00110	99·98790
	Altenau...	0·00700	0·00490	0·00200	0·00080	0·00100	99·98430
ENGLISH REFINED LEAD.							
London Lead Company. *Best selected*		0·02360	0·00580	0·00210	0·00180	0·00100	99·96570
Pontifex and Wood. *Selected*		0·07580	0·00320	0·00220	0·00320	0·00200	99·91360
W. Blackett. *Best selected*		0·03180	0·00590	0·00170	0·00370	0·00500	99·95200
CARINTHIAN AND SILESIAN LEAD.							
Villach, Carinthia		0·00210	0·00520	0·00250	0·00320	trace	99·98700
Stolberg, near Aix-la-Chapelle		0·03830	0·00500	0·00240	0·00180	0·00250	99·95000
Friedrichshütte, near Tarnowitz, Prussian Silesia. Desilverized by Pattinson's process		0·00130	0·00220	0·00800		0·00150	99·98700
Tarnowitz lead contains[1]	according to Löwig	..	..	0·02	0·03	..	99·21
	according to Ziurek	..	..	0·018	..	..	99·883

[1] Berg- u. hüttenm. Zeit. 1866, p. 84.

Composition of German and Spanish Lead.

Locality and Date of Production.	Copper.	Antimony.	Arsenic.	Iron.	Nickel.	Cobalt.	Manganese.	Zinc.	Cadmium.	Bismuth.	Silver.	Lead.	Analyst.
Eschweiler Company, near Stolberg 1867	0·0501	0·0021	..	0·0008	..	..	..	..	..	0·0020	0·0044	99·9406	Fresenius.
Do. Do. 1869	0·00187	0·00248	..	0·00066	0·00092	..	..	..	..	0·00365	0·00100	99·98942	Fresenius.
Herbst and Co., Call, Rhenish Prussia 1867	0·0051	0·0015	..	0·0020	0·0010		trace	..	..	..	..	99·9874	Fresenius.
Do. Do. 1870*	0·00045	0·00070	..	0·00210	..	..	..	..	..	0·00235	0·00050	99·99360	H. Rœssler.
Pirath and Jung, Commern 1869	0·00268	0·00921	trace	0·00121	..	..	..	..	0·00083	..	0·00275	99·98329	Fresenius.
Mechernich Company 1869	0·00243	0·00118	trace	0·00090	0·00075	..	..	..	..	..	..	99·99474	Fresenius.
Do. 1870†	0·00230	0·00310	..	0·00170	..	..	..	0·00260	..	..	0·00055	99·98975	Fresenius.
Fadé and Co., Braubach 1869	0·00190	0·02639	trace	0·00129	..	..	..	trace	..	0·00553	0·00385	99·96104	Fresenius.
Real Compania Asturiana 1868	0·00057	0·00133	trace	0·00124	trace		trace	0·00308	..	0·01041	0·00010	99·98597	Fresenius.

* Desilverized by zinc, and the lead dezincified by fusion under chloride of lead. This lead contained a trace of thallium.
† Desilverized by zinc, and the lead dezincified by smelting with tap-cinder in a blast-furnace.

COMMERCIAL DETAILS.[1]

Purchase of Ores.

In Flintshire "ticketings" were held twice a month, but now are only held once. The Miners intending to sell give notice to the Smelters, who send their samplers to take samples, which are put into water-proof bags, as no allowance is made for moisture in the ore. The samples are assayed by the Smelter by the iron-dish process. The highest bidder at the ticketing becomes the purchaser. The ore is weighed at the Mine, and carried away at the cost of the purchaser. Many of the smaller Mines sell to the Smelters by private contract according to a given Standard, say, a certain price for ore yielding 77% of lead by assay in the iron-dish, and if the price fixed upon for such Standard ore be 14*l.* per ton, the actual price paid would vary with the actual produce, the ore being taken to the Smelting-Works and there weighed and assayed. Under such an arrangement, formerly, if the ore produced 80%, the price paid would have been 14*l.* 15*s.* per ton,—if 70%, 11*l.* 5*s.*; but at present more than 11*l.* 5*s.*, and less than 14*l.* 15*s.*, would be given for ores of those respective produces.

In Cornwall, Cardiganshire and partly in Denbighshire, the Isle of Man and elsewhere, each Mine sends samples of its ore to the Smelters in various localities, along with a notice to the effect that tenders or tickets will be received up to a certain day, on which they will be opened and the highest offer accepted. Copies of all the tenders received are sent to each Smelter. In all these cases the ore is sold dry, in some by the statute ton of 20 cwts., and in others by the ton of 21 cwts. Some Mines will sell at one month's credit, and others at 2 or 3 months'; but all these particulars being notified to the Smelter, the sum which he bids is regulated accordingly.

Cost of Smelting in the Flintshire Furnace in Flintshire.

The Smelter, in estimating his profits, has to take into account the gross value of the pig-lead and the silver contained in the ore, less carriage to the Smelting-Works, loss of lead in smelting, cost of smelting, interest on capital, and other obvious conditions. The cost of smelting a ton of lead-ore varies, of course, with the price of labour and fuel, percentage of lead, nature of the ore, and other circumstances; but the average cost of smelting good Flintshire ore in the reverberatory furnace, inclusive of reducing the slags, is estimated by Mr. Keates at 18 shillings per ton of ore. This, however, is irrespective of the cost of extracting silver, which varies with the proportion of this metal in the ore, and with other circumstances.

[1] For the following information on this subject I am indebted to my friend, Mr. Keates.

LIST OF BRITISH LEAD-SMELTERS IN 1870.

ENGLAND.

CHESHIRE :—
The Runcorn Smelting Company, Runcorn.

CORNWALL :—
Treffry's Executors, Par, Cornwall.
Mitchell and Company, Truro, Cornwall.

CUMBERLAND :—
The London Lead Company, Nenthead, Alston Moor.
W. B. Beaumont, Allendale, Alston Moor.

DERBYSHIRE :—
Benjamin Bagshaw, Eyam, near Bakewell.
Barker and Rose, Alport, Bakewell.
Joseph Wass and Son, Lea Lead-Works, Matlock Bath.
Gibbs and Company, Bonsall Dale, Matlock Bath.
E. Cockburn, Meer Brook, Matlock Bath.
" Via Gellia Works.
J. Fairburn, Sheffield Works, near Chesterfield
Robert Howe Ashton, Castleton.

DURHAM :—
E. Backhouse, Darlington.

LANCASHIRE :—
Peter Glover, Warrington.

NORTHUMBERLAND :—
Shield and Dinning, Haydon Bridge.
W. J. Cookson and Company, Newcastle.
Locke, Blackett, and Company, Newcastle.
Howden Smelting Company, Newcastle.

SHROPSHIRE :—
Snailbeach Company, near Shrewsbury.
Pontesford Smelting Company.

SOMERSETSHIRE :—
Treffry and Company, Mendip Hills Lead Company.
Thomas Somers, Bristol.
Sheldon Bush and Panther Smelting Company, Bristol.
Weston and Collingborn, Bristol.
East Harptree Lead-Works Company, Limited, East Harptree.[1]
St. Cuthbert's Lead-Smelting Company, Limited, near Wells.[1]

WESTMORELAND :—
Greenside Mining Company, Greenside, near Penrith.

YORKSHIRE :—
Keld Head Mining Company, Keld Head, Wensleydale.
George York, Pateley Bridge.
Duke of Devonshire, Grassington.
C. L. Bradley and Company, Hurst, Blakethwaite, and Swaledale.
Lister, Robinson, and Company, Grinton Moor.
R. M. Jaques and Company, Arkengarthdale.
G. Robinson, Surrender.
R. M. Jaques and Company, Old Gang.

[1] The above firms are not buyers of lead ores in the open market, but smelt ore and slag, both derived principally from the heaps of débris left by the Romans. There is at present scarcely any lead-mining proper in the Mendip district.

WALES.

CAERMARTHENSHIRE :—
Sims, Willyams, Nevill, and Company, Llanelly.
The Bury Port Smelting Company, Pembrey.

DENBIGHSHIRE :—
Delafield Smelting Company, near Wrexham, late Brymbo Company.

FLINTSHIRE :—
Adam Eyton, Llanerchymor, Holywell.
Walker, Parker, and Company, Dee Bank and Bagillt, near Holywell.

GLAMORGANSHIRE :—
Stock and Company, Penclawdd, near Swansea.

SCOTLAND.

DUMFRIES :—
Duke of Buccleuch, Wanlock Head.

LANARKSHIRE :—
Lead Hills Mining Company, Lead Hills.

IRELAND.

WICKLOW :—
Mining Company of Ireland, Ballycorus.

QUANTITY OF LEAD ORE, LEAD, AND SILVER, PRODUCED IN THE UNITED KINGDOM OF GREAT BRITAIN AND IRELAND IN 1868.

Extracted from the Mineral Statistics of the Museum of Practical Geology.

Counties.	Lead Ore.		Lead.		Silver.
ENGLAND.	Tons.	Cwts.	Tons.	Cwts.	Ozs.
Cornwall	8,415	16	6,310	9	303,033
Devonshire	1,522	12	1,141	0	39,865
Somersetshire	1,135	0	606	0	..
Derbyshire	5,933	0	4,395	18	1,150
Staffordshire	115	14	86	15	..
Lancashire	441	0	326	10	1,580
Shropshire	4,942	18	3,823	0	..
Yorkshire	7,693	16	5,654	12	2,500
Cumberland	5,520	5	4,097	4	33,057
Westmoreland	2,053	11	1,388	8	21,314
Durham and Northumberland	23,720	17	17,805	8	81,447
WALES.					
Cardiganshire	7,230	14	5,414	10	67,502
Caermarthenshire	500	0	375	0	2,153
Pembrokeshire	294	0	220	10	2,860
Montgomeryshire	4,019	9	3,049	13	19,546
Merionethshire	56	0	41	0	202
Denbighshire	8,266	0	6,382	5	33,370
Flintshire	4,321	10	3,255	0	29,808
Carnarvonshire	238	9	180	11	700
ISLE OF MAN	4,290	0	3,089	5	178,718
IRELAND	2,089	0	1,562	10	14,372
SCOTLAND	2,436	13	1,811	13	8,201
Total produce of the United Kingdom of Great Britain and Ireland	95,236	4	71,017	1	841,328

Summary for Five Years ending 1868.

	Lead Ore.	Lead.	Silver.
	Tons.	Tons.	Ozs.
1864	94,463	67,081	641,088
1865	90,452	67,251	724,856
1866	91,051	67,391	636,688
1867	93,432	68,441	805,394
1868	95,236	71,017	841,328

Production of Lead in Various Foreign Countries.

Country.	Year.	Tons.
Spain	1866	66,803
German States	1867	49,337
Island of Sardinia	1867	23,255 [1]
France	1864	16,692 [2]
Belgium	1867	10,352
Greece	1869	8,483 [3]
Austro-Hungarian Empire	1867	7,637
Sweden	1868	284

[1] This amount is computed from the return of lead ore exported, estimating it at 70% produce.
[2] This amount includes the produce of a large quantity of foreign ores imported from Sardinia and elsewhere.
[3] This is the amount imported into the United Kingdom from Greece, not the total production. It is sold at Newcastle in lots of from 500 to 1000 tons, and is there softened. Grecian lead is said to be chiefly derived from old slags, and to contain from 16 to 20 ozs. of silver per ton.

Table showing the Quantity of Lead Imported into the United Kingdom and Exported therefrom in 1868 and 1869.[4]

	1868.	1869.
	Tons.	Tons.
Foreign lead imported	58,731	62,218
Ditto exported	580	998
Net import of lead	58,151	61,220
British lead exported	51,459	51,688
Excess of imported lead retained	6,692	9,532
Native produce of lead	71,017	
Apparent total consumption of lead in the United Kingdom	78,789	

[4] Compiled from the Customs' returns. The lead is estimated in the metallic state, and the amount calculated in the litharge, red-lead, white-lead, and lead ore imported, the average proportion of lead in litharge and red-lead being taken as 90%, in white-lead as 80%, and in lead ores as 70%.

MISCELLANEOUS DETAILS.

Cast Sheet-Lead.

In former times the sheet-lead used for roofing and other purposes was obtained by casting; and in my boyhood I have often seen the process conducted, as nearly as I can recollect, in the following manner.[1] There was a rectangular and solidly-constructed table of wood, usually about 5′ wide and 20′ long, not unlike a billiard-table, having a raised border 4″ or 5″ high, except at one end where the surplus lead flowed off. The top of this border on each side was perfectly smooth, somewhat rounded off at the edges, and parallel to the surface of the table, which had a very slight inclination from one end to the other. At the higher end of the table was a trough, of the same width as the table, and so arranged, that by means of a lever and chains, it could be hoisted and tilted in such a manner that when filled with molten lead, the metal would flow in a broad sheet over the table. The trough was of wood coated with a thin layer of sand, but one of iron was subsequently used.[2] Near this end of the table was a large cast-iron melting-pot set over a furnace, in which the lead intended to be cast was melted, and from which it could be conveniently laded into the trough. At the lower end of the table was a gutter inclining from one side to the other to receive the superfluous metal and convey it into a cast-iron pot, mounted on wheels, placed underneath. The table was covered with a layer of fine sand duly tempered with water so as to cause it sufficiently to cohere when beaten down. The sand was riddled, shovelled over the table, and distributed evenly and solidly, and after each casting the same operation was repeated. The instrument used for levelling and beating down the sand was called a "strickle," which is represented in the annexed woodcut (fig. 144). It consisted of a narrow piece of wood about 5″ deep and

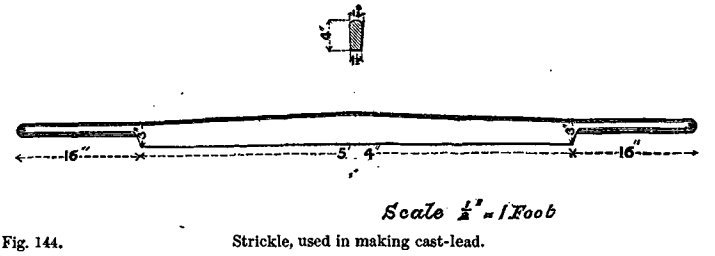

Fig. 144. Strickle, used in making cast-lead.

2″ thick, considerably longer than the width of the table, and rounded off at each end for convenience in handling. In preparing the bed, it was placed across the table at right angles and manipulated by

[1] A short and pretty accurate description of the operation of casting sheet-lead will be found in the interesting and instructive volumes on the Manufactures in Metal in Lardner's Cabinet Cyclopædia, London, 1834, vol. 3, p. 63. The foregoing description has been corrected and a sketch of the strickle supplied by Mr. Rhodes of Nottingham, the plumber whom I often saw engaged in casting lead.

[2] Such troughs were also made of cast-iron or of strong sheet-iron rivetted.

two men, one at each end, who worked synchronously, first levelling the sand and then beating it down from one end of the table to the other. The surface of the sand was afterwards smoothed by means of a sort of plasterer's trowel of copper. Immediately after pouring the lead, the lower or narrow side of the "strickle," after having been wiped clean and greased, was drawn rapidly over its surface from the top to the bottom of the table, in order to remove the superfluous metal. Variation in the thickness of the lead was usually produced by slight extra moistening of the sand and by casting the lead rather cooler. By this means the strength of the lead could be varied from 6 to 8 lbs. per foot. The thickness of *plate-lead* as it was termed, used for pumps, was varied by nailing pieces of leather of suitable thickness round the handles of the "strickle," where they slided on the borders of the table, and casting on a perfectly level surface. Considerably more lead was poured over the table than sufficed to produce a sheet, and before pouring from the trough, it is hardly necessary to state, that the metal was carefully skimmed and precautions taken to prevent as far as practicable any dross from becoming intermixed with the flowing metal. Immediately after casting, the receiving-pot at the lower end of the table was wheeled up to the original melting-pot, and the lead which it contained, while still liquid, was laded into that pot; the sheet was cut square at the ends, then rolled up and removed.

The Chinese, it is stated, prepare their well-known tea-lead by casting, notwithstanding its thinness. "Two men are employed: one of them is seated on the floor, with a large flat stone before him, and with a moveable flat stone-stand at his side. His fellow-workman stands beside him with a crucible containing the melted lead; and having poured a sufficient quantity on the slab, the other lifts the moveable stone, and placing it suddenly on the fluid lead, presses it out into a flat and thin plate, which he instantly removes from the stone. A second quantity of lead is poured on in a similar manner, and a similar plate is formed; the process being carried on with singular rapidity. The rough edges of the plates are then cut off, and they are afterwards soldered together for use. Mr. Waddell, a Scotchman, who witnessed the operation in China, applied a similar method, with great success, in the formation of thin plates of zinc for galvanic purposes."[3]

Rolled or Milled Sheet-Lead.

The process of rolling, or, as it was originally termed, milling lead, appears to have been first practised in England in 1670, when a Company was formed for carrying it on.[4] An Act of Parliament

[3] Lardner's Cabinet Cyclopædia, antea cit. p. 65.

[4] The following details are derived from a curious little volume entitled "The New Invention of Mill'd-Lead, for *Sheathing of Ships* against the *Worm*, better for *Sailing*, and Cheaper above *Cent. per Cent.* than the old way with *Boards*," etc. London, 1691.

was obtained, granting to the Company a monopoly of this "Manufacture, Art, or Invention," of which it was alleged, the chief and most important application was to "preserve Ships, and other Vessels under Water." By command of the King, Charles II., several ships of war (about twenty) were sheathed with milled-lead. The results, according to most of the official reports, were unsatisfactory, owing mainly to the great and rapid corrosion of the iron-work, especially the bolts and rudder-irons, which had been in contact with the lead; but Sir John Narbrough was of opinion that the corrosion was due to the copper covering the rudder-irons, and the copper-nails used to attach the sheathing. The Company, however, asserted that the ordinary practice of protecting iron-work, intended to be overlaid with sheet-lead, namely, painting it with a mixture of tar and hair, had been designedly omitted in sheathing the ships with milled-lead; and that, consequently, the results were vitiated. By an order of Council, at the Court at Whitehall, December 22, 1682, the King himself being present, an enquiry was directed to ascertain whether lead-sheathed ships do suffer greater damage in their iron-work than those sheathed with wood, or not at all; and if so, the reason.

The Company seem to have possessed their full share of worldly wisdom, and to have been adepts in the art of procuring highly favourable testimony to the value of their sheathing from officials at Portsmouth, Chatham, Woolwich, Sheerness, and Deptford. Of the nature of that art an indication is afforded by the following statement published by the Company:—

"The Lords of the Admiralty's Commission being determined, before they had proceeded to make any Report herein, and King *Charles* the second taking in (*sic*) to himself the Office of *Lord High Admiral of England*, which was transacted by his Brother, Mr. *Pepys* being Secretary, and Sir *Anth. Dean* and Mr. *Hewer* (the one always a professed Friend to the Thing, and the other not only so, but to that time a Partner also for a twelfth share in the Work) being made *Commissioners of the Navy*, the Mill'd-Lead Company could not but expect their *Lead-sheathing* would soon be *restored* by the Power of these Gentlemen," etc. (p. 58).

In spite of the Company's "Printing, Proofs, or Proposals," they could not prevail upon His Majesty's "Officers for *Building* and *Ordnance*" to adopt milled-lead instead of cast-lead, notwithstanding they offered to supply it at less than the cost of the latter; and the reason assigned for their failure is, that it was "against the Inclinations or Profit of the Plumbers and their Friends, who had Power or Interest enough to hinder the admittance thereof into the King's Works." The Plumbers, who made and used cast sheet-lead, had a vigorous encounter in print with the Company, each party disparaging the article manufactured by the other. Inequality of thickness, cracking, cockling, and unsoundness from blow-holes, are set forth as the special defects of cast sheet-lead. On the other hand, the Plumbers, in a communication to the Navy-Board, thus expressed themselves with regard to milled-lead: "The Mill'd-Lead is noways so serviceable

and cheap as the same is represented, nor indeed scarce fit for any service, as is evidently proved by daily experience in most places where the same has been used; that after it hath lain a few Years, it hath crack'd, flaw'd, and rose in ridges, so that the Persons concerned, after having been at a considerable Charge in the daily patching and mending of it, have at last been forced to take it up, and lay Cast-Lead in the room of it, before such time as the Houses or Places could be made tight: of the truth of which, several Examples can be given your Honours upon Oath, if required. That on the other side, the Cast-Lead doth plainly make appear its durance and service, for in several old Buildings about this City and *Westminster*, where this Lead hath been laid for a great term of years, (it) yet remaineth as firm and right as when first laid: And besides, the same is cheaper and better to their Majesty, or any private person, by 20*l. per Cent.* than the Mill'd-Lead is, according to the Rates it is now sold, which together with the strength and service is very considerable. Also the Solder made and used by them of the Mill'd-Lead is not fit for service, whereas all Solder used by the Plumbers is by Essay scaled according to the standing Rules of the Company. By what is here offered, is humbly desired may be taken by your Honours, as proceeding from Duty [let the reader mark this noble disinterestedness], and not in prejudice to the Persons concerned in the Mill'd-Lead, for notwithstanding the plausible pretences of the usefulness and service of the said Lead, and the disparagement of the Cast-Lead, yet the Plumbers have not made any like returns to discredit the Mill'd-Lead, not for want of reasons, but being assured that a short time would sufficiently make appear the service and firmness of the Cast-Lead, and the sleightness and the charge of the other, which is now sufficiently evidenced, and is humbly submitted to your Honours' Consideration" (p. 102).

Then follows an enumeration of places where milled-lead had been used and is said to have been taken up very soon afterwards. The Company, nothing daunted, issued a rejoinder containing certificates from the owners of several of the buildings mentioned, or of their agents, flatly contradicting the allegations of the plumbers, which were pronounced to be "Scandalous and false." Here ends this little history of a fierce contention between rival manufacturing interests, which teaches a lesson of practical wisdom, as much needed now as in the 17th century. The moral, according to the Milled-Lead Company, is that "All New Inventions (being proposed as better and cheaper, to lay aside something before used for the same purpose) must expect to meet with great Opposition; for some particular Persons, and some Trades which consist of many Persons being concern'd in Point of Interest, right or wrong, they will decry that which is against their profit, and procure as many others as they can to do so too" (p. 93). But, it may be asked, is not this charge in many cases equally applicable to the introducers of novel manufacturing operations?

Casting lead for rolling.—The metal is poured into open moulds of

cast-iron, so as to form large square or rectangular slabs several inches in thickness. After solidification, a slab, while it may be yet hot, is passed backwards and forwards through the same pair of rolls, which, consequently, are fitted with reversing gear; but many manufacturers allow it to cool previously, and make a dozen castings before beginning to roll. The metal as it leaves the rolls is supported on a series of wooden rollers, having their axes in the same horizontal plane and parallel to those of the rolls; and there is a series of such supports extending for a considerable length on each side of the rolls. When the slab is reduced in thickness to a certain degree, it is divided into pieces of such dimensions as are necessary to produce the kind of finished sheets required; each piece is then rolled separately. When thin sheets are made, two or more sheets are placed one upon another and rolled together. If in rolling any depressions are observed on the upper surface of the slab, little bits of sheet-lead are placed in front of those depressions, so as to force the subjacent lead into them and fill them up; and as soon as the bits of lead have served this temporary purpose, they are taken off. The same slab of lead may be passed through the rolls 200 or 300 times. I was struck with the concavity presented by the ends of the slab while undergoing the operation of rolling; from which it clearly appears that the metal near the surfaces extends, or as it is now termed, flows, in greater degree than the central portion, the reverse of what occurs in rolling slabs of iron. But in the latter case the central portion is much hotter, softer, and consequently more yielding, than the external; whereas in a slab of lead which is rolled cold, this condition does not exist, and in one which is rolled hot it exists only in a comparatively slight degree.

In casting lead it is not necessary to stir the metal in the melting-pot; for, by properly melting it, impurities rise to the surface, which, before tapping, is skimmed clean. The lead should be just hot enough to admit of being skimmed, but not so cold as to cause it to stick to the iron tools, such as bars, which are used in the operation; otherwise, rich skimmings are obtained and the casting is unsound. If at the commencement of melting, the pot should be made red-hot, the accumulated heat will suffice to melt the charge without the addition of fresh fuel, and the temperature of the metal will generally be found right for tapping. However, if the lead after fusion be too hot for skimming, it must be cooled either by opening the fire-door or by adding cold lead. While the lead is running on to the "bed," which consists of a plate of cast-iron, it rushes down the "spout," termed launder, with great force against the bed-frame, often bursting through and causing inconvenience and loss. In order to prevent this evil, the force of the stream was lessened or checked by holding an iron rake against it. Five or six years ago, the following alteration in the mode of tapping was introduced by Mr. Hughes, and is regarded by him as a great improvement: a sheet-iron launder, having a circular spout at one end directed downwards at right angles, conveys the lead from the tap-hole to the centre of the bed, whence

it spreads itself equally all over it; this arrangement saves the necessity of using an iron rake for diffusing the metal, and is stated to ensure a far better casting. But it should be added, that the advan-

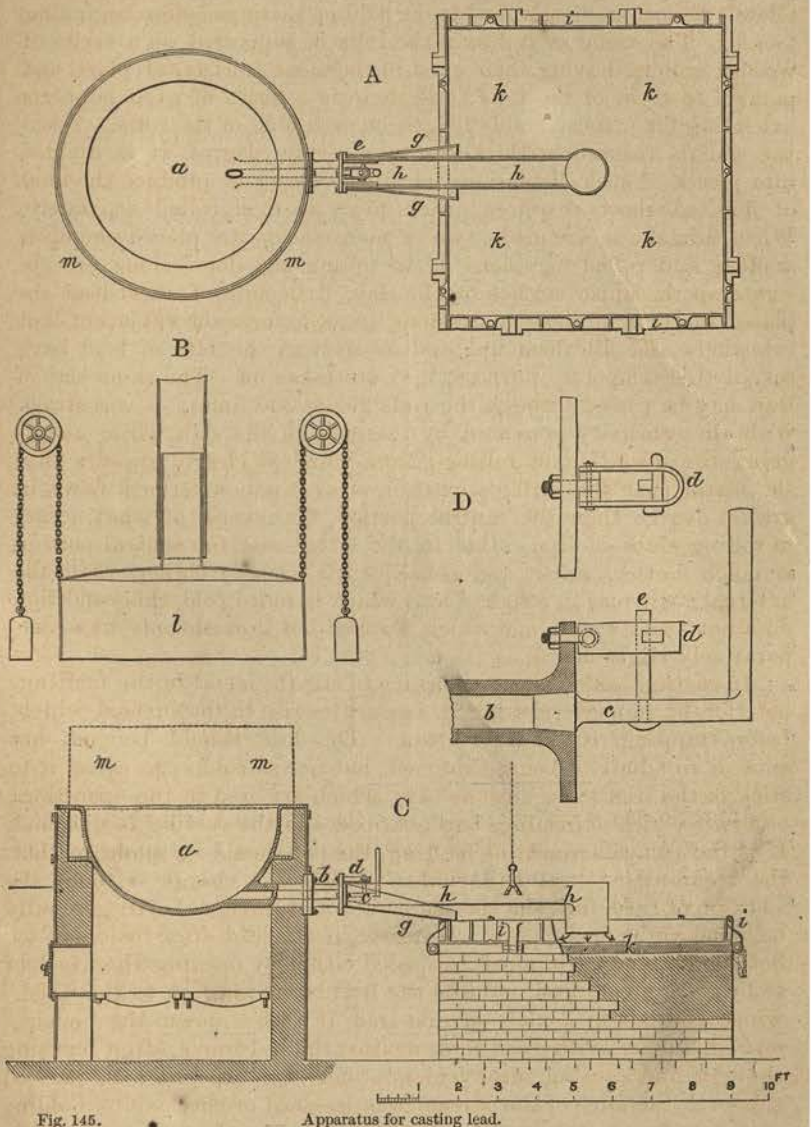

Fig. 145. Apparatus for casting lead.

tage of this alteration is not generally admitted. As soon as the melting-pot is emptied, the cast-lead is carefully skimmed with a wooden skimmer, of the same width as the bed, and held by two men, one at each end, who draw it over the surface of the molten metal, and

repeat the operation until its surface has become quite clean. The bed and sides are not washed over with anything, as that is needless. Some manufacturers line the sides of the bed with timber, because sheets with better edges are thereby obtained, and a little scrap is saved; but the value of the timber burnt counterbalances that of the scrap saved. Formerly, lead was laded into the middle of the bed during cooling, in order to prevent too much sinking in the centre; and this was then required, because the bed was sometimes quite level all over or convex through bad moulding of the iron-founder. But by making it slightly concave, that evil was obviated. The average weight of a cast plate of lead is 8½ tons.

The details of the apparatus above described are represented in fig. 145, prepared from drawings supplied to me by Mr. Thomas Hughes, and re-drawn by Mr. William Prim.

Description of fig. 145:—

A. Plan of the melting-pot and casting-bed.
B. Moveable hood over the melting-pot.
C. Vertical section, and part elevation, of the melting-pot and casting-bed through the centre.
D. Plugging arrangement, scale of ¾″ to the foot. *The general scale applies only to* A, B C.
a. Melting-pot of cast-iron, resembling an ordinary Pattinson-pot in construction and mode of setting. It is 1½″ thick in the centre, and tapers to ¾″ at the rim. The brickwork of the furnace is completely surrounded with sheets of iron ¼″ thick, which are kept together by the usual iron bands, 3″ broad and ¼″ thick, and wrought-iron uprights.
b. Flanged pipe, 3″ in bore, cast on the pot.
c. Plug of wrought-iron, accurately fitted to the mouth of the pipe (*b*), and adjusted by means of the strap (*d*) and the pin (*e*).
g. Launder made of sheet-iron, ⅛″ thick, intended to receive any overflow of lead from the launder (*h*).
h. Launder made of sheet-iron, ⅛″ thick, to carry the molten lead from the melting-pot to the centre of the bed (*k*).
i. Cast-iron frame, 7″ deep, forming the sides of the bed. This frame is in four pieces, of which each is on two hinges. It is made moveable, so that the slab of cast-lead may be conveniently withdrawn. The pieces of the frame are fastened together at the corners with screw-bolts; and there are also other bolts which pass vertically through the frame-pieces into the bed (*k k k k*). See A., C.
k k k k. Cast-iron bed, slightly concave, 7′ 5″ long, 7′ broad, and 3″ thick.
l. Hood of sheet-iron, 1/16″ thick, counterpoised with three weights, and moveable up and down, as shown in B. In the middle at the top there is a wrought-iron pipe 1/16″ thick, working within another similar pipe, connected either with a chimney, or passing through the roof of the building, as may be most convenient. The chief object of the hood is to carry off the effluvia produced, especially in melting old lead; and by covering the charge it also facilitates fusion.
m m. An iron sheet, ¼″ thick, fixed on the side of the pot from *m m*, of which the object is to prevent loss of lead while charging, when often a quantity of molten metal is splashed about, the metal being thrown in from the opposite side, and the hood of course being kept raised during that operation.

According to Mr. Thomas Hughes, the rolls used in making sheet-lead are always "grain rolls," cast in loam, and the dimensions of ordinary rolls are shown in the woodcut, fig. 146, from a sketch supplied by Mr. Hughes.

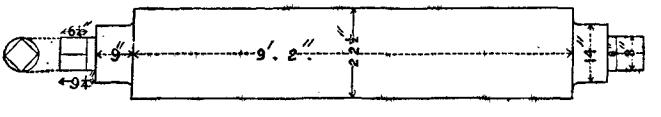

Fig. 146. One of a pair of rolls used in rolling lead.

Lead suitable for Pipes.

According to a manager of great experience in the manufacture of lead, soft desilverized lead is the best for pipes, which when wholly composed of it resist greater pressure of water than those made of a mixture of it and inferior lead. Pipes formed by melting together

soft pig-lead and old lead, having a little solder attached, are stiffer and brighter than those made entirely of the former, and are much liked by plumbers, because they are not so liable to flatten and enable them to make what is termed a "neat job." At one large establishment pipes are never, but sheets are always, made wholly of soft lead. For large pipes some slag-lead may be added in order to increase their stiffness. During many years, Messrs. Newton, Keates, and Company, employed tea-lead exclusively for their Composition Gas-pipes, which were very hard and stiff.[1] England having introduced thin sheet-lead into China to supersede Chinese tea-lead, old tea-lead came to consist of a mixture of the Chinese and English articles; and the result was, that pipes produced from such a mixture were softer, darker in colour, and less uniform in quality than the old pipes previously made of genuine Chinese tea-lead. Subsequently the plan was adopted of melting all tea-lead in a coke fire, and allowing it to trickle therefrom into an iron pot, from which it was laded into pig-moulds. The pigs of lead thus procured were melted in admixture with old lead of fair quality and old solder-joints; and from this metal nice bright pipes were obtained, which gave general satisfaction. At a large establishment pipes, which plumbers approve of, are composed of a mixture of 1 part of tea-lead, melted as above described, and 5 parts of desilverized lead. A Birmingham Firm adds antimony to the lead, which it uses in the manufacture of Composition Gas-pipes, in order to render them sufficiently hard and bright. It is asserted that such expedients as those above mentioned are merely resorted to in order to satisfy the whims of different customers.

Lead suitable for Sulphuric Acid Chambers.

The purest lead, *i.e.* the softest, is stated to have been found best for Sulphuric Acid Chambers; but a very observant manufacturer of that acid informed Mr. Keates, that soft lead, obtained direct from good ores, is more durable, in his opinion, for such chambers than soft desilverized lead.

Lead suitable for Red-lead to be used in the Manufacture of Flint-glass.

The red-lead, supposed to be best for the manufacture of flint-glass, and which sells for about 5% more than other red-lead, is prepared from lead obtained from the ore of the Snailbeach Mine, in Shropshire, on the borders of Montgomeryshire. Opinion seems to be now divided on the subject of the alleged superiority of this article for the purpose in question, as has been previously intimated. Comparative freedom from copper is certainly one characteristic of red-lead most suitable for the manufacture of flint-glass.

The following determinations of the proportion of copper in Snailbeach lead have been made in my laboratory:—

[1] Bishop Watson states that a Congo chest of tea contained about 10 lbs., and a Hyson chest about 4 lbs. of tea-lead. Chemical Essays, 1782, 3. p. 358.

PROPORTION OF COPPER PER CENT. IN SNAILBEACH LEAD.

0·0055
0·0065
0·00525
0·00525
0·0021

Nickel and cobalt were specially sought for, but none was detected. The proportion of copper in lead smelted from the same parcel of ore and in the same furnace may vary sensibly in the metal obtained in successive tappings.

LEAD SUITABLE FOR WHITE-LEAD.

The best white-lead, *i.e.* the whitest, was supposed by many to be made from what is known in the market as "W.B. selected and refined" pig-lead (the initials being those of Walter Blackett, the producer, and now applying equally to the name of his successor, Wentworth Beaumont). This pig-lead is the produce of certain mines on the Greenwich Hospital Estate, in the North of England, which are leased to Mr. Beaumont; it fetched a higher price, to the amount of from 5% to 7½%, than any other pig-lead. So great was the prepossession in favour of this pig-lead for the manufacture of white-lead, that attempts to persuade London white-lead manufacturers to make a trial of the best and purest soft lead from other sources were fruitless, notwithstanding it was offered at about 30*s.* per ton, *i.e.* 7½% less than W. B. lead. Commercial competition, however, seems at length to be uprooting prejudices which, as in the case in question, have probably no better foundation than traditional credulity. It is to be hoped that now-a-days the world is growing wiser, and will judge an article of manufacture by its quality and not by its pedigree. Many illusions connected with articles of manufacture have been dispelled in recent years, with much gain to the public, and, possibly, it will be found that plenty of lead is produced in Great Britain and elsewhere quite as suitable for conversion into white-lead, as that bearing the mark "W.B. selected and refined."

MANUFACTURE OF RED-LEAD.

History.—This pigment was known to the ancients. Under the term minium Pliny certainly included cinnabar and red-lead; and he states that the practice existed of adulterating the former more valuable substance with the latter—a fraud not yet extinct, as some years ago I found minium in the red crayon of an artist, which ought to have contained only vermilion. He speaks of barren stuff accompanying silver and lead ore, which became red when heated in furnaces, and on being afterwards triturated to powder constituted the inferior kind. "Steriles etiam plumbi deprehenduntur solo colore nec nisi in fornacibus rubescentes exustique tunduntur in farinam. Hoc est secundarium minium perquam paucis notum."[1] Davy infers, and probably with reason,

[1] Naturalis Historiæ, Lib. xxxiii. cap. vii. sect. 40. Sillig's edition, 1851, 5. p. 107.

that this sterile stuff was native carbonate of lead.[2] Moreover, Pliny informs us that minium was prepared by the calcination of white-lead or ceruse; that it was discovered by accident in a fire that occurred at the Piræus, where jars containing ceruse had been heated; and that Nicias, an artist, was the first to employ it in painting. "Usta casu reperta est in incendio Piraeei, cerussa in orcis cremata; hac primum usus est Nicias."[3] Davy detected red-lead amongst the substances contained in a large earthen vase filled with mixtures of different colours with clay and chalk, which was found in a chamber in the baths of Titus.[4]

General principles.—The process of manufacturing red-lead comprises two distinct stages, the first in which lead is converted into protoxide, and the second in which the protoxide is converted into red-lead, the sole agent of oxidation in both being atmospheric oxygen aided by suitable heat. In the first stage the temperature should be considerably below the melting-point of protoxide of lead, and in the second it should be considerably lower than in the first. The first stage is in some localities termed "drossing," and the product "dross." The second stage is in some localities termed "colouring," and the product "colour," and as these words seem to me convenient, I shall use them in the sequel. In some works both operations are conducted alternately in the same oven; while in others two ovens differing but slightly in construction are employed, named "drossing" and "colouring" ovens respectively. The ovens in use at the present day are substantially the same as in former times. The woodcuts 147 to 150 inclusive, represent the red-lead "colouring" ovens of my friend Mr. Adkins, at Smethwick, near Birmingham, to whom I am indebted for drawings both of his "drossing" and "colouring" ovens. As these ovens closely resemble each other, the construction of the former will be easily understood from the woodcuts and description of the latter.

Drossing-oven.—The oven is a low-arched furnace, having a bed slightly inclining from each side towards the median line, and 7″ from back to front. This bed is made of brick, and is supported by a bed-plate of cast-iron, resting on the side-walls and intervening piers of brick. The bed-plate has raised borders on each side and at the back, and may be described as a shallow box without a front. There are three openings in front fitted with hinged doors of cast-iron, one on each side, of the same dimensions for introducing the fuel, and a central larger one through which the oven is charged with lead and rabbling is effected. The top of the central doorway is a little higher than that of the side doorways, whereby, owing to this slight difference in height, the entrance of air through the side doorways is promoted as well as the escape of the gaseous products of the combustion of the fuel from the upper part of the central doorway. At an equal distance from each side of the oven a low vertical wall or fire-bridge extends along the bottom from front to back, and the spaces included between these walls

[2] The Collected Works of Sir Humphry Davy, 1840, 6. 138.

[3] Op. cit. Lib. xxxv. cap. vi. sect. 20.

[4] Op. cit. 6. 135.

and the adjacent sides of the oven respectively constitute two fire-places, without any grate. The length of the bed from back to front in the clear is 11′, and the width between the bridges, where they are parallel, is 8′ 4″. Immediately underneath the middle door is a space, of which the sides are formed of two vertical plates of cast-iron, the back by the lower part of a large cast-iron plate supporting the front of the oven and containing the central doorway, and the bottom by the floor here covered with a plate of cast-iron, the front and top being left open. This space receives the oxidized lead as it is drawn out at the end of the first or drossing stage. In front of the oven above is an arched space or hood of brickwork, prolonged upwards into a short vertical chimney; and the products of the combustion of the

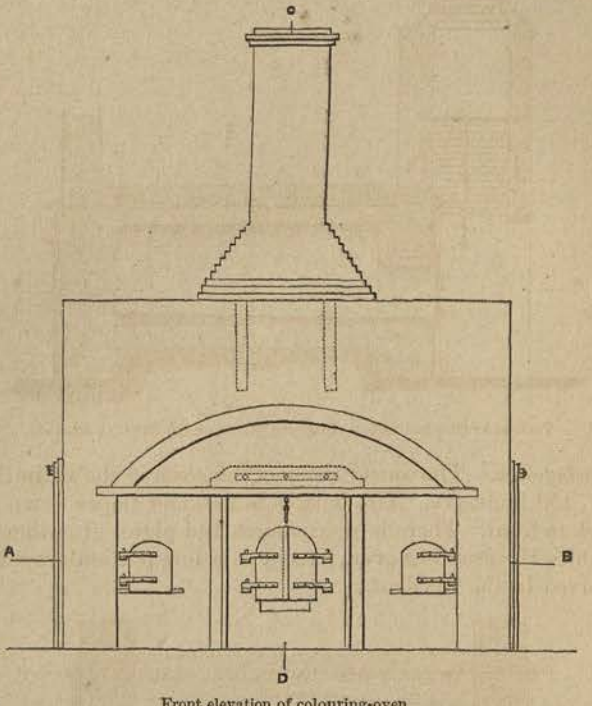

Fig. 147. Front elevation of colouring-oven.

fuel or other vaporous matters, which may escape from the oven, ascend through this hood. In front of the central door a chain is suspended having a hook at the bottom, which serves as a fulcrum for the rabble. The oven is firmly braced by means of cast-iron standards and wrought-iron tie-rods, as shown in the woodcuts. The fuel in such an oven is always coal in lumps of considerable size; but in many ovens the fire-places are provided with grates and ashpits extending backwards for about one-third of the length of the oven, and in that case coal in small pieces or even slack may be employed. The oven, it will be observed, resembles a baker's oven, and has no inlet or outlet except in front.

Fire-brick should be used as the internal lining, as well as for the bottom. The top of the oven is covered with a layer of badly conducting material, such as sand.

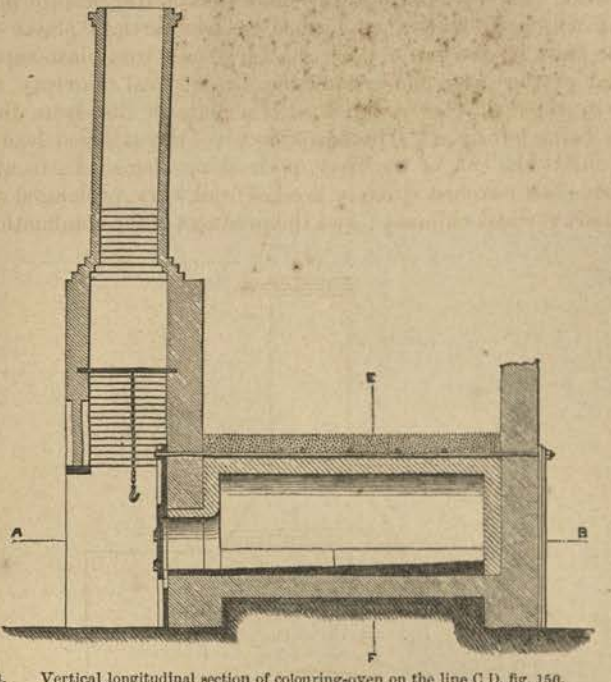

Fig. 148. Vertical longitudinal section of colouring-oven on the line C D, fig. 150.

Colouring-oven.—The construction of this oven is shown in the woodcuts 147, 150 inclusive. The bottom is flat, and slopes down 4 inches from back to front. There is no cast-iron bed-plate. In other respects it resembles the drossing-oven, except in a few particulars which will be perceived in the woodcuts.

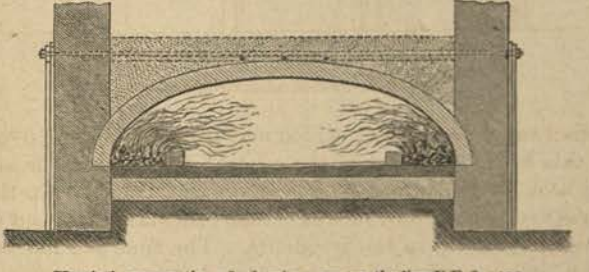

Fig. 149. Vertical cross-section of colouring-oven on the line E F, fig. 150.

A modification in the form of red-lead ovens, which is adopted in several red-lead works, is shown in figs. 151, 152. This oven, it will be observed, is provided with fire-grates.

The tools employed in the processes of drossing and colouring are represented in figs. 153, 154.

I am indebted for details of the process of manufacture to Mr. W. Baker, formerly manager of the lead-works of Messrs. Rawson, Barker and Co., Sheffield, to Mr. Heron, of the lead-works at Ballycorus in Ireland, and to Mr. Keates, formerly one of the proprietors of the lead-works at Holywell, Flintshire; and to the same sources I am also indebted for working drawings of red-lead ovens. I may add that I have had the opportunity of witnessing the process at several works.

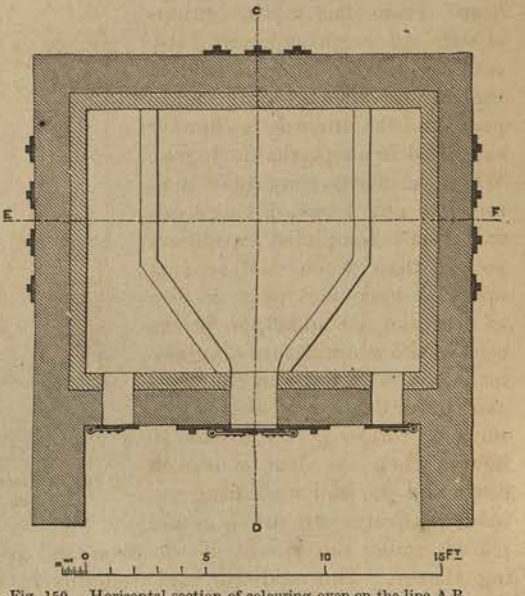

Fig. 150. Horizontal section of colouring-oven on the line A B, figs. 147, 148.

Description of the process as conducted at the works of Messrs. Rawson, Barker and Co., Sheffield. — The following description is by Mr. Baker. The floor of the oven is made of pressed fire-bricks laid edgewise: it slopes downwards from the back towards the centre $\frac{1}{2}''$, thence to the mouth $1\frac{1}{2}''$, and from the sides towards the median line $\frac{1}{2}''$.

At 6 A.M. the oven is charged with 22 cwts. of pig-lead, including about 1 cwt. of lead which had remained unoxidized and been drained off from the previous charge. The molten lead is kept in by a dam across the floor of the oven in front, and the material used for this dam consists of the coarse particles of intermixed lead and protoxide of lead obtained in grinding and levigating the product of a former charge, which is technically termed "leanings" (a local corruption of the word leavings); it is beaten down firmly with a strong flat piece of wood. The lead quickly melts, and forms a pool behind the dam. In about two hours after the fusion and continual rabbling of the

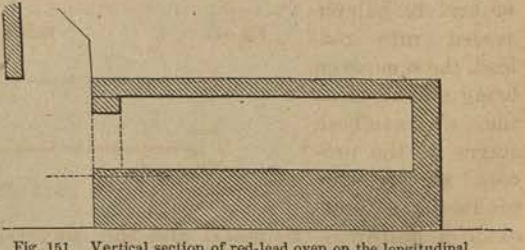

Fig. 151. Vertical section of red-lead oven on the longitudinal median line.

molten metal, the oxide which has been formed is thrust into a heap towards the back of the oven. The workman continues to splash the molten lead over this heap with a quick jerking movement of the rabble, which is suspended by the chain in front of the oven, and at intervals of half an hour to transfer the freshly-formed oxide to the heap. From time to time lumps of slag-lead weighing about 2 lbs. each are thrown into the pool of lead where the rabbling takes place, and the drossing is thereby expedited in a remarkable degree. When the charge consists of *common lead* and 1 cwt. of slag-lead, oxidation is completed two hours sooner than when *best lead* is operated upon and only 28 lbs. of slag-lead are added, as is the case in the manufacture of glass-makers' red-lead. The charge is oxidized or drossed, or, as it is also termed, "dusted," in about 10 hours, when the dam is broken down and the lead remaining unoxidized drains out into a mould placed under the mouth of the oven, and is added to the succeeding charge. The oxidized lead remains in the oven until 3 A.M. the following morning, when it is raked out and wetted with water where it lies upon the floor in front of the oven. A plank is placed on the moistened heap to form a "run" upon which the men walk as they now proceed to charge the oven with the ground and levigated oxide of lead to be converted into red-lead, the same oven being employed at these works in both stages of the process, namely, the production of protoxide of lead from the metal and the conversion of that oxide into red-lead.

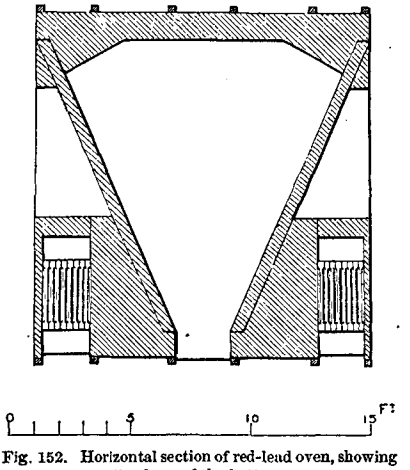

Fig. 152. Horizontal section of red-lead oven, showing the form of the bottom.

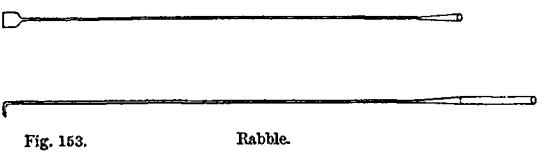

Fig. 153. Rabble.

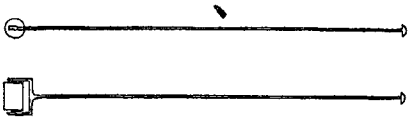

Fig. 154. Stone roller.

The preparation of the product of the first stage for its further oxidation into red-lead is conducted as follows. It is conveyed into a tub or trough lined with lead, from which it is supplied to adjoining grit-millstones, rotating horizontally just like those of a flour mill, in which it is ground. A stream of water is kept flowing into the stone's eye, which is regularly fed with the product from the tub. The stuff

as it issues from the stones in the state of greenish-yellow mud flows into a conical-shaped vessel termed "a puddler," in which a shaft with vertical arms of metal attached revolves. By this means, as well as by the aid of a force-pump which supplies water at the bottom of the "puddler" and causes a constant overflow from the top, the finer particles are kept in mechanical suspension, and carried over through a long spout into settling tanks. The finer particles thus removed are yellow, while the coarser, which remain in the "puddler," are greenish, consisting of particles of metallic lead encrusted with protoxide: it is the latter which are used for making the dam in front of the oven, as before stated. If protoxide of lead in fine powder be required, the deposit in the settling tanks is merely dried in the oven and then passed through a sieve; the dried oxide has a reddish-buff colour. But if red-lead be required it is kept heated in the oven during about 48 hours, the temperature being carefully regulated all the while and the mass frequently rabbled. When the proper tint of red-lead has been attained, the charge is drawn out of the oven, left to cool, and afterwards passed through a sieve. Orange-lead is made by similarly heating white-lead and the froth which is obtained in the process of grinding and levigating white-lead. With a considerable proportion of froth the resulting orange-lead is in a very fine state of division, and feels very soft under the palette-knife. According to Mr. Baker, an orange-tinted red-lead may be procured by leaving the first product (PbO) of the oxidation of pig-lead exposed to the air until some carbonate of lead has been formed by the absorption of atmospheric carbonic acid, and then heating it as usual in the second stage. The quantity of carbonate, so formed, will, *cæteris paribus*, depend upon the length of exposure and the extent of surface exposed. Mr. Baker states that particles of metallic lead may be detected both in red-lead and the finely-divided protoxide.

The process as conducted by the Mining Company of Ireland at Ballycorus.—The description communicated by Mr. Heron, of the Ballycorus Lead Works, differs in some respects from that of Mr. Baker. The charge is 25 cwts. of lead. Rabbling is continued incessantly during the first 5 or 6 hours, when almost the entire mass will have become converted into oxide. The charge is now raked towards each side of the oven in equal proportions, leaving a channel in the middle by which any lead remaining in the metallic state may drain off. The temperature up to this point is stated to be that of "faint redness," but now it is increased, and the charge is turned at intervals of 2 hours. The chief object in this part of the process is to oxidize the remaining particles of lead and sweat out what will not oxidize. The dross is withdrawn from the oven, and when cold is ground and levigated. The apparatus employed for this purpose is represented in the annexed woodcut prepared from a lithograph supplied by Mr. Heron.

When the ground dross enters the bran-tub, those particles that are heavy enough to resist the onward flow of the water fall to the bottom and there remain, while the other part is carried forwards

into the settling-vat, where it also gradually subsides. This part of the stuff must be ground so fine as not to produce the least feeling of grittiness when rubbed between the fingers. The deposit in the bran-tub, which consists of intermingled particles of metallic lead and protoxide, is returned to the oven, heated during 8 or 10 hours, and afterwards again ground and levigated. After the subsidence of

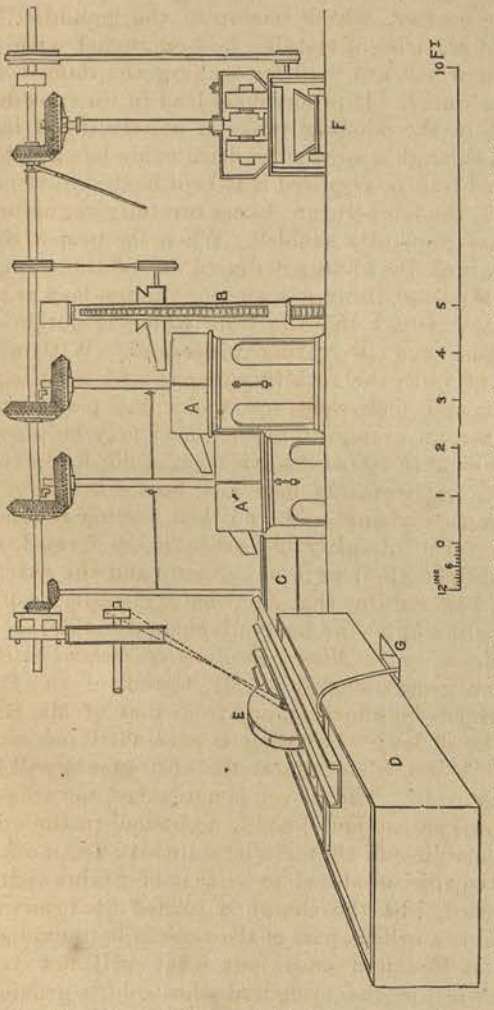

Fig. 155. View of the interior of the Ballycorus Works, showing the machinery used in grinding and levigating.

A A'. Two pairs of millstones.
B. Endless belt with small tin buckets attached, which revolves on pullies, and carries up the stuff to the hopper of the stones A. A small stream of water is allowed to trickle into the centre of the stones whilst in motion, by which means grinding is facilitated, and the ground stuff, escaping in the state of mud from the stones A, is carried into the second pair of stones A', from these into the bran-tub C, and finally into the settling vat or depositing-vat D, both previously filled with water.
C. A round tub, having a vertical spindle rotating in the centre. To this spindle arms are attached with chains hanging from them, the dragging movement of which keeps the water in constant agitation. At the Holywell Works, Mr. Keates states that a piece of stone was fitted into the bottom of the bran-tub, upon which another piece of stone was made to revolve by means of an upright shaft, whereby the dross was kept in agitation.
D. A long rectangular vat into which the water, with mechanically suspended matter, flows from the bran-tub C; a stream is made to flow back into the same tub C by a small Persian wheel E, so that the water is kept in constant circulation.

the stuff in the settling-vat D, the supernatant water is drawn off by a syphon into a cistern G, after which the moist deposit is laded into an iron handbarrow and conveyed into an iron shoot into the second or colouring-oven, which differs only from the drossing-oven in having a flat bottom instead of an inclined one. Any fine particles which may be carried over through the syphon are subsequently recovered

in the settling-vat. The charge is from 35 to 40 cwts. It quickly becomes dry, when a small stone roller (fig. 154) is passed over it in order to crush any lumps which may have been formed during desiccation. [In the north of England they are careful to leave all lumps uncrushed, as these colour soonest and keep the charge open. This may seem strange, but it is true. In moving the charge from time to time the air gets all round the lumps.' The same remarks hold true of colouring orange-lead.—*From a Correspondent.*] After this the whole duty of the furnace-man is to maintain the temperature as uniform and at as nearly the right degree as possible, and to turn the charge over frequently, so as to promote the absorption of oxygen by exposing fresh portions to the direct action of the air. At the expiration of 48 hours the charge is drawn out into an iron waggon. A sample of the charge should be examined every 12 hours, when a change of shift takes place, in order to ascertain whether the proper advance in colour has been made. When cold the product, which is bright red, requires to be riddled. For this purpose it is fed into the machine F. fig. 155, which consists of a pair of iron edge-rolls enclosed in a case, in order, as far as practicable, to prevent the escape of red-lead dust into the atmosphere, and so lessen the liability to sickness incident to men employed in the manufacture of red-lead. The red-lead thus ground falls through a fine wire sieve, working underneath the edge-rolls, into a waggon placed to catch it. The process is now completed, and all that remains is to pack it in casks for sale.

The increase in the weight of the lead is found to be from 7% to 8%, inclusive of the loss in manipulation. The maximum theoretical increase should be 10·36%, *i.e.* 100 parts by weight of lead should yield 110·36 of red-lead. The red-lead manufactured at Ballycorus has been analysed and found to have the following composition per cent.:—

Peroxide of lead (PbO^2)	18·89
Protoxide of lead (PbO)	80·54
Sesquioxide of iron	0·19
Copper and silver	trace.
	99·61

Observations on Mr. Adkins' red-lead.—The lead used by Mr. Adkins for the manufacture of red-lead is that from the Snailbeach mine, Shropshire; and no red-lead has been held in greater local repute by flint-glass makers. The excellence in quality for that purpose has been attributed to the freedom of Snailbeach lead from copper. Formerly red-lead suitable for flint-glass makers was manufactured from lead derived from the Bog Mine, also in Shropshire; but in the course of working, probably in a new lode, lead was raised which ceased to be applicable to that purpose, and Bog Mine lead was accordingly abandoned. Some years ago a complaint proceeded from the flint-glass makers respecting the quality of red-lead made from Snailbeach lead. The glass was reported not to be so bright and

clear as it should have been. A sample of this lead was examined in my laboratory by Mr. Tookey with the following results. It contained traces of iron, copper, silver, and gold; but not a trace of tin, antimony, arsenic,[5] or cobalt could be detected. However, I saw a specimen of galena from the deepest level at that time being worked, and from which the lead complained of had been raised, with which was associated cobalt bloom (arseniate of cobalt) in spots. By cupellation the lead yielded 2 ozs. 0 dwt. 12 grs. of silver per ton, containing a trace of gold.

At Mr. Adkins' works the ground and levigated protoxide, there technically called "casing," was put while moist into the colouring-oven and heated during 24 hours, a high colour not being desired.

I observed a considerable quantity of white and greenish deposit on the roof of the drossing-oven at the same works, which is stated to have been caused by the splashing of the lead, and its subsequent oxidation. An analysis of this substance is given at p. 520.

Drossing by machinery.—At some works a vertical shaft with metal blades or wings attached is fixed in the centre of the oven, of which the bottom is oval or dish-shaped. When the shaft revolves the pool of lead is kept in agitation by the blades, and the oxide of lead produced is heaped all around by means of the rabble. It has been asserted that several tons of lead can thus be operated upon at a time, but this is probably incorrect, and only a few cwts. more than the average charge can be so treated.

Mode of action of slag-lead in the process of drossing.—Pigs of slag-lead may be easily recognized when struck with a hammer by the sharp sound or *ring* which they emit as compared with pigs of soft lead; and long ago it was rightly conjectured that slag-lead owed its hardness and ring to the presence of foreign metals or other matters, especially antimony. Now it has been demonstrated that this metal is generally, if not always, present in slag-lead, and that soft and pure lead may be rendered hard and in other respects to resemble slag-lead, particularly in whiteness, by the addition of a small proportion of antimony. Experiments have conclusively proved that pure lead alloyed with an extremely small proportion of antimony expedites the process of drossing in a remarkable degree. In 1867 a friend of mine, largely engaged in lead-smelting, showed me in my laboratory the following interesting experiment. Practically pure lead, weighing 9600 grains, was melted in a plumber's metal-pan or wrought-iron ladle, raised to dull redness and stirred actively with an iron rod. Drossing took place, but slowly. After a few minutes 1 grain of antimony, previously alloyed with a few grains of lead, was dropped in, when, as though by magic, the metal was immediately affected on continuing to stir it, and the whole mass in

[5] An experienced friend is nevertheless convinced, and it may be with reason, that it *certainly* contained traces of antimony and probably of arsenic.

the course of a few seconds became pasty from oxidation on the surface; and the formation of oxide proceeded with a rapidity which I should hardly have believed possible without ocular proof of the fact. In the course of some minutes the effect of the antimony seemed to be exhausted, and drossing took place slowly as at first. The repetition of another dose of antimony was instantly followed by the same result as occurred after the first dose. My friend assures me that $\frac{1}{30000}$ of antimony suffices to produce the effect above described, though the drossing does not take place quite so rapidly, It is one of the most striking and instructive experiments I have ever seen, and is particularly interesting as showing how the presence of a minute quantity of another metal may affect the oxidizability of lead. The lead employed in the experiment above recorded had been prepared by my friend on a large scale from selected ores, and with especial care for experiments on pure lead, or the nearest approach that can be made to it, regardless of expense.

Mr. W. Baker states that lead containing sulphur may be advantageously substituted for slag-lead in the manufacture of red-lead; and he has communicated to me the following information on the subject. On examining slag-lead from Derbyshire, he found that it contained both antimony and sulphur. He melted in two crucibles, such as are used in the melting of steel at Sheffield, 1 cwt. of good soft lead and added 2% of pure galena. It was poured out while red-hot, and during solidification it passed through a pasty condition, as does common plumber's solder (an alloy of lead and tin) or ordinary slag-lead. It was, however, not white, as is lead alloyed only with antimony; and, when broken while sufficiently heated to be frangible, its fractured surface was granular, and presented the purple and yellow colours characteristic of lead free from antimony. Baker asserts that their red-lead maker found his artificial sulphuretted slag-lead to act as well as the usual slag-lead. Careful experiments have been made on this subject at other British lead-smelting works, which have led to the conclusion that sulphur has only a slight drossing action.

According to Baker *soft* lead containing from 10 to 20 ozs. of copper per ton oxidizes in the red-lead oven more readily than purer lead, shortening the process sometimes by as much as 2 hours. He has also observed that the oxidation goes on more quickly when, after the formation of a certain quantity of protoxide, the latter is banked up so that the rabble splashes the molten lead over it; and he suggests that it might be desirable to leave in the oven a portion of the dross from the preceding charge in order to hasten oxidation in the next. The experience of some other lead-smelters is opposed to Baker's opinion as to the drossing action of copper; and, indeed, his own results stated below are also opposed to that opinion. Whatever substance may be used to promote drossing must be added gradually; for it is oxidized faster than the lead, and either slag-lead or antimony must be added in order again to start the action. But Baker

found much more copper in the lead left unoxidized in converting a charge of lead into red-lead than existed in the original lead, thus showing concentration of copper (see the numbers underneath indicated by A and C).

Concentration of copper in the lead remaining unoxidized.—Baker has made observations on this point, of which he has furnished me with the following particulars. Samples were taken

(A) Of the charge of lead		27 cwts.
(B) Of the slag-lead		1 ,,
(C) Of the returns, *i.e.* of the metallic lead tapped off at the end of the day's work.		4 ,,
(D) Of the red-lead made.		
A contained of copper in 500 grains	0·199	grain.
B ,, ,,	0·273	,,
C ,, ,,	0·329	,,
D ,, ,,	0·185	,,

Baker computed that the proportion of copper in the red-lead should be 0·180 gr. in 500 grs., which agrees nearly with the result found on analysis.

Accidental production of red-lead.—In 1847 I received from Plattner interesting specimens of red-lead taken out of the culverts of an iron-smelting blast-furnace at the Asbach Smelting Works in Rhenish Prussia.

Concretionary matter in making red-lead.—Bishop Watson gives the following account of this substance in his Essay on Red and White-Lead:—"During the making of red-lead, part of it is volatilized; there rises up from it a vapour, which attaches itself to the roof of the furnace, and forms solid lumps. These lumps are of a yellowish-white colour, mixed with pale green and some reddish streaks, wherein are frequently small red crystals, resembling such as may be artificially formed by subliming sulphur and arsenic together. The workmen call the whole of what is separated from the lead, in the form of smoke, sulphur: when this sublimed matter is detached from the roof of the furnace, the red parts are converted, by a subsequent process, into red-lead; and the yellow ones are sent to the smelting-furnaces, to be run down again into lead. The quantity of this sublimate amounts to about 5 cwts. in making 100 tons of red-lead. The proportion here assigned is not wholly to be relied on, since the smoke arising from the lead forms itself into larger masses and in less time, when it is not constantly swept from the roof of the furnace than when it is; and the workmen endeavour to keep the roof as free from it as they can, because a small portion of it injures the colour of a large quantity of the red-lead with which it happens to be mixed." From Watson's description, it appears that drossing and colouring were performed in the same oven.[6]

At an inspection of Mr. Adkins' red-lead ovens in 1850, I collected

[6] Chemical Essays, 1782, 3. p. 343.

a specimen of the concretionary deposit on the roof of a drossing-oven, which has been analysed by Smith in my laboratory (1870). It is porous, friable, and somewhat like calcareous tufa in appearance. Its prevailing colour is white, with a pale buff tinge; but in some parts it is pale green, and in others pale blue; a little brownish-red matter may also be observed. When heated to redness it melts, and while hot its colour is yellow, and when cold it is a crystalline mass of a yellowish tint; but the powder of the mass is much lighter in colour, being nearly white. At my request, my friend Professor Miller, of Cambridge, has examined this substance, and favoured me with the following notice respecting it:—"I cannot discover any definite crystals in it. The reflexions are from convex surfaces, not from planes. Under the microscope, with transmitted light between crossed Nichol's prisms, the larger portion remains dark. Here and there, however, a small quantity of coloured light comes through, as if a few crystals were mechanically mixed with a large quantity of some other matter in a vitreous condition. But I have not been able to isolate any crystals. Judging by the colour, the copper appears to be very unequally distributed through the substance."

Composition of Concretionary Matter from Drossing-Oven.

		Oxygen.
Protoxide of lead	87·73	6·29
Sulphuric acid	11·68	6·99
Protoxide of copper	0·005	
Iron	trace	
Silver	0·0002	
Water and traces of carbonic acid	0·40	
	99·8152	

500 grains of the substance yielded by dry assay a bead of silver, which weighed 0·001 grain, and corresponds to 1 dwt. 7 grains per ton. Manganese, zinc, nickel, cobalt, antimony, and sulphurous acid were sought for, but none could be detected by operating upon 100 grains. The composition of this substance is approximately represented by the formula $PbO,SO^3 + 2PbO$, which (taking PbO = 112) corresponds to the following composition per cent.:—

Protoxide of lead	89·36
Sulphuric acid	10·63

It may, therefore, be regarded as tribasic sulphate of lead; and its mode of formation is probably as follows:—A deposit of protoxide of lead is first formed, and then slowly converted by the sulphurous acid resulting from the oxidation of the pyrites in the coal used as fuel, into basic sulphite of lead, which, by the prolonged action of heated atmospheric air playing over it, is changed ultimately into basic sulphate.

Poisonous effects of the manufacture of red-lead.—This is a subject

which in these days of sanitary improvement has of late excited attention, and precautions, far from satisfactory however as yet, have been adopted for the preservation of the health of the workmen. In the sifting,[7] grinding, and packing of red-lead it becomes more or less diffused through the atmosphere, as is testified by the appearance of the walls and roof of the building devoted to those operations; and the inhalation of the air so contaminated will give rise to the usual symptoms of lead-colic. Not only in that case do particles of the red-lead pass into the lungs, but also into the stomach, being washed down along with the saliva and mucus of the mouth and fauces which must become impregnated with the poison. Efficient ventilation will probably be found to be the most practical and least expensive remedy for the evil in question.

EROSION AND PERFORATION OF LEAD BY INSECTS.[1]

Lead has been found to be irregularly eroded or perforated, and in some cases in such a manner that at first sight local electrical action, due to intermixed foreign matter, might reasonably be suspected as the cause, and blame, accordingly, be ascribed to the smelter or manufacturer. On this account a notice of the erosion and perforation of lead by insects is not out of place in a treatise on Metallurgy. In 1833, Audouin exhibited to the Entomological Society of Paris, sheet-lead deeply grooved from the roof of a building; and in 1844, Desmarest read a paper before the same Institution, in which he mentioned the erosion and perforation of sheet-lead by a species of coleopterous wood-borer, *Bostrichus capucinus*, and at the same time he showed specimens of cartridges from the Arsenal at Turin in illustration of the same fact. In 1843, M. Du Boys, of Limoges, presented to the Agricultural Society of that town specimens of type-metal (*clichés*) riddled with holes, which were regarded as the work of insects. The French observed in the Crimea during the war that some of their cartridges were singularly eroded, and an official enquiry was instituted as to the cause. Some of the bullets were simply grooved superficially, while others were pierced through and through with holes 3 or 4 millimetres (0·12″ or 0·16″) in diameter. In 1858, Marshal Vaillant exhibited specimens of these bullets to the Academy, which had been brought from the Crimea. The Russians did not observe the phenomenon in their cartridges. Scheurer-Kestner, in 1861, published an account of the erosion of the lead of a new sulphuric acid chamber; and the insect, which was hymenopterous, was caught in the act of escaping in its perfect or imago state through the lead, having been imprisoned between it and a wooden support.

The effect observed in the Crimea has been clearly traced to the larvæ of the *Sirex gigas*, a well-known hymenopterous insect, which lives in the interior of old trees or pieces of wood, and which in the

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[7] Many manufacturers do not sift their red-lead.

[1] I have obtained information on this subject chiefly from the following sources: Comptes Rendus, 1857, t. 45; 1858, t. 46; 1861, t. 53.

perfect state might be mistaken for a kind of wasp. It has not yet been found in the Crimea by Russian entomologists; but it occurs in England, Sweden, Germany, and in the Jura in France. It attacks certain kinds of fir-trees. It erodes the lead with its mandibles, reducing it to powder, but eating none of it. The insect was doubtless contained in the wood of the boxes of cartridges imported by the French into the Crimea. Specimens of cartridges gnawed like those in the Crimea, and in which insects of the same species had been found *in situ* were submitted to the Academy by M. Bouteille, Curator of the Museum of Natural History, at Grenoble. Similar perforations in lead have also been traced to *Callidium sanguineum*, of the order Coleoptera. Pouchet, writing in 1867, announces that he had recently examined a piece of the gutter of a church, which presented numerous perforations produced by a species of Callidium.[2]

I have been informed that a mysterious and startling humming sound having been heard to proceed from the interior of a piano, it was found to be caused by an imprisoned *Sirex*, which had passed its larva stage in the wood of the instrument.

In 1839, while at Matlock Bath, in Derbyshire, I received from the late Mr. Melville, of the then cotton-spinning firm of Arkwright and Melville, specimens of sheet-lead, curiously perforated, which had served as the lining of wooden troughs used for soaking cotton in water. It was stated that the entire lining of the troughs soon became thus acted upon. The perforations were first perceived about a year after the troughs had been lined. The troughs were circular, and the width of the lead-lining, measured flat, I find to be $6\frac{1}{4}$"; and the holes are nearly all included within about the middle third of the lining. The perforations are numerous, varying from about $\frac{1}{8}$" to somewhat less than $\frac{1}{16}$" in diameter; some are so round and regular that they might have been drilled, while others are more or less irregular; and what is worthy of note, they are all, so to speak, counter-sunk on the same side of the sheet. There are also numerous minute circular pits, which occur only on the side of the sheet where the countersinking appears, or that which had not been in contact with the wood. I ascertained that the mill, in which the perforations had occurred, was supplied with water from the Mill-Stone Grit formation; and that no perforations had been observed in another mill, supplied with water from the Carboniferous Limestone, although it was believed that the lead used in both cases was identical in quality because it had been procured from the same source. The troughs were made of red Petersburgh deal. The edges of the pieces of sheet-lead were soldered together. The water was conveyed in leaden pipes into a leaden cistern, from which it was drawn. There had been no change in the troughs, the water, the cotton, or in anything since the first use. The perforations were not regularly distributed, but were more numerous in some parts than others. In a letter which Mr. Melville wrote to me, dated January 27, 1840, is the

[2] The Universe. Translated from the French. London, 1870. p. 210.

following sentence:—"If I may be allowed to hazard a conjecture, I should say it is possible that the small insect, which is common in timber, may have perforated the wooden trough, and coming in contact with the lead may have worked its way through that also." But the fact of the countersinking and pitting being confined to the outer side of the sheet which had been in contact with water and not with the wood of the trough is opposed to this view.

POISONING BY LEAD.

Circumstances in which Poisoning by Lead is apt to occur.—Persons engaged in metallurgical operations of which lead is the subject, such as smelting and cupelling; in the manufacture of compounds of lead, such as red-lead and white-lead; in painting with pigments of lead, like house-painters; in mixing red-lead with the other ingredients required for the production of flint-glass; in manipulating with pottery glazes containing oxide of lead,—are liable to poisoning by lead. Cases have also been published in which the frequent handling of metallic lead or its alloys is stated to have produced poisoning; but such cases seem to have been extremely rare.[1] The symptoms of this poisoning are the same as those which result from the habitual use of drinks containing a compound of lead in solution or in suspension. Lead may be introduced into the system through the lungs by inhalation of lead-smoke or of air contaminated with plumbiferous dust; through the stomach by swallowing food or drink impregnated with lead; and through the skin or mucous surfaces by prolonged contact with lead, or with various substances in which it exists, such as lotions and ointments.

Dr. Christison considers it probable that all the preparations of lead are poisonous, except the metal, and perhaps also the sulphide. What seems a reasonable supposition is, that every compound of lead which is capable of being absorbed from mucous surfaces or the skin, and diffused through the system, will produce poisoning; and if this be so, the question arises whether there are compounds of the metal, such as the insoluble sulphate and sulphide, which are incapable of such absorption and diffusion, and are, therefore, innocuous. This is an important practical subject of enquiry with reference to preventive as well as remedial measures; and, indeed, special methods of treatment have been proposed and adopted in the belief that there are such innocuous compounds of the metal. Experiments such as giving dogs strong doses of metallic lead or sulphide of lead prove little; but the repeated exhibition of either of these substances in small doses would shew whether sufficient of the metal would be dissolved, however slowly, to enter the system and cause poisoning.

It seems to be a disputed point whether working in lead-mines produces poisoning, some authors maintaining very positively the affirmative, and others as positively the negative. In favour of

[1] This statement is fully confirmed by the experience of Messrs. Clowes and Sons, at their large establishment where this volume was printed.

the latter view, Dr. Christison cites the authority of Mr. Braid, who was for some years surgeon at Leadhills, in Lanarkshire, where galena is raised, and who found that the miners never had the colic until they worked at the smelting-furnaces. I am informed by Mr. James Williams, who has had large experience as the medical attendant of the works of Messrs. Walker, Parker, and Co., and others where lead is the subject of treatment, and of many lead-mines in the vicinity of Holywell, that he has never seen a case of lead-poisoning amongst the miners, notwithstanding even carbonate of lead in many of those mines is associated in considerable quantity with the galena raised. But supposing galena not to be hurtful to health, yet carbonate of lead, if inhaled in the state of dust, would assuredly in the course of time occasion the disease.

Symptoms of Poisoning by Lead.[2]—The chief symptoms are severe griping pain in the belly and obstinate constipation; and the disease is termed Lead-Colic or Painter's Colic. One of the most remarkable and conspicuous premonitory signs of poisoning by lead is that of a blueish-grey line along the gums at their junction with the teeth; and this appearance which—strange to say, was only first detected not many years ago—has received the name of Blue-gum.[3]

The pain in Lead-Colic may be pretty constant, intermittent or remittent; and is generally, but not invariably, relieved by pressure. The belly is almost always hard, the abdominal muscles being contracted; it is sometimes rather full, but usually the reverse, the navel being often drawn in so as almost to touch the spine. There is either no discharge from the bowels, or scanty hard lumpy fæces are passed with much straining and pain; and, in a few instances, it is stated, there is diarrhœa instead of constipation. The urine is commonly diminished in quantity, while the saliva is increased and has a blueish tint. From the first, but more frequently after a few hours or days, pain is felt in the head and limbs—especially the inside of the thighs, knees, calves of the legs, ancles, and soles of the feet—accompanied sometimes with cramps, and sometimes even with epilepsy and coma.[4] The countenance is dull, anxious, and gloomy; and in advanced cases the expression of gloomy anxiety is said to exceed that in almost all other diseases. There is great

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[2] The works which I have chiefly consulted are the following:—The Cyclopædia of Practical Medicine, 1833, 1. p. 442; Watson's Lectures on the Principles and Practice of Physic, 1843, 1. p. 447; Christison's Treatise on Poisons, 1836, p. 513; Andral's Clinique Médicale, by Dr. Spillan, 1836, p. 882; Die metallurgischen Krankheiten des Oberharzes, von Dr. Carl Heinrich Brockmann, Clausthal, 1851, p. 227.

[3] The local synonyms of this disease are Devonshire Colic, Belland in Derbyshire, Madrid Colic, and Dry Belly-ache in the West Indies. In scientific nomenclature it was formerly designated *Colica Pictonum, i.e.* Colic of Poitou, the old French province, from its being epidemic in former times amongst the inhabitants of that country (in Latin, *Pictones*), on account of their drinking wines adulterated with sugar of lead. But in the nomenclature of diseases adopted by the Royal College of Physicians in London (1869), it is termed *Colum ex plumbo* or *Colum pictorum*.

[4] Mr. Williams informs me that he has never seen a case accompanied with epilepsy or coma.

prostration. The pulse is rarely quickened and often retarded, a febrile condition being quite exceptional. The skin has a dull, dirty, cadaverous appearance; it is frequently, but not uniformly, hot, and in either case, it is bedewed with irregular, clammy perspiration. The disease may occur abruptly, while the patient appears to be in good health, but it is usually preceded by impaired appetite, indigestion, and restless nights. By-and-bye the uneasiness, originally confined to the stomach, extends to the whole abdomen, and the stomach becomes so irritable that eating is followed by vomiting. Cramps in the pit of the stomach succeed, and before long occur over the rest of the belly, the disease being then fully developed.[5]

Course of the disease.—By timely and proper treatment, the patient usually recovers as from ordinary colic in less than eight days. But the disease is apt to recur when the patient again exposes himself to the conditions which induced it in the first instance. Individuals, however, differ much in susceptibility of poisoning by lead. Sir Thomas Watson records a remarkable case, within his own experience, in which a patient first became affected with Lead-Colic after working with white-lead for nineteen years. It is said that a patient who has once suffered from Lead-Colic becomes more liable to the disease upon exposure to the exciting cause. In subsequent attacks of this disease, either before or after recovery, local palsy or fatal apoplexy may supervene. The seat of the palsy is the hands, which hang dangling down when the patient stretches out his arms; it is the extensor muscles which are chiefly affected, so that the fingers and thumb are flexed and contracted upon the palm. This symptom characterizes the disease appropriately termed Wrist-drop or Drop-hand. The palsied muscles waste, and the result is most apparent in the ball of the thumb. But patients often recover completely even from this affection. If, however, they resume their trade and persist in exposing themselves to the same noxious conditions as previously, they will become miserable cripples, and, according to Sir Thomas Watson, sink under some visceral disease. Such are the usual effects of poisoning by lead; first comes the colic, perhaps several times, and then the palsy. But it is asserted that instances of Wrist-drop occur without having been preceded by colic. According to my friend, Dr. Rees, senior physician of Guy's Hospital, this is not unfrequent; and in one such instance, which came under his observation, the subject was a gentleman poisoned by taking snuff impregnated with lead. According to Dr. Christison, compositors are rarely attacked with Lead-Colic, but are, it is believed, subject to partial palsy of the hands from their frequently handling type-metal; and he states that he had met with one case apparently of this kind. Lead-Colic is seldom fatal as colic; and in the rare cases in which death has taken place from coma or otherwise during the disease, no appearances have been discovered on *post-mortem* examination, which afford the least explanation of the pain or constipation.

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[5] In this description I have in the main adopted Dr. Christison's language.

Poisoning by lead is said to predispose to gout;[6] and Amaurosis[7] and Albuminuria[8] have in some instances been ascribed to the same cause.

Absorption of lead and its diffusion throughout the body.—Although it might reasonably be assumed, that in poisoning by lead the metal is absorbed and diffused throughout the body, yet assumption is unnecessary; for it has been demonstrated by experiment that such is the fact. The metal has been detected by chemical analysis in the palsied muscles and in the brain of man,[9] as well as throughout the carcases of animals killed by slow poisoning with it; but why, as Sir Thomas Watson remarks, it fastens solely or chiefly on particular muscles, or particular nerves, nobody knows. Blue-gum is regarded as a proof of the absorption of lead, and is supposed to result from the conversion of the compound of lead circulating through the system into sulphide of lead, but how has not been ascertained with certainty. In cases of poisoning from frequently handling or otherwise manipulating metallic lead, minute particles of the metal and the superficial tarnish of oxide, which quickly results from atmospheric air, are doubtless conveyed from the fingers to the food and so pass into the stomach.

Treatment of Lead-Colic.—I am indebted to my friend Dr. Owen Rees for the following account of the treatment which he follows at Guy's Hospital, where numerous cases of the disease are received. In the majority of cases an ounce of castor-oil, mixed with 10 drops of laudanum, is given twice daily, and large hot poultices of linseed-meal are applied to the belly. At night a draught consisting of 40 drops of Battley's sedative solution (Liquor opii sedativus) in camphor-mixture, is prescribed, if the bowels have been acted upon by the oil taken during the day. In severer cases, accompanied with tenderness of the belly and retching, bleeding from the arm to the amount of 16 or 20 fluid-ounces may be practised with advantage when the patient is young and strong. Pain and spasm are thereby very quickly allayed, and the stomach often loses its irritability, and, immediately afterwards, retains food and medicine. When the patient is less robust, the application of 15 or 20 leeches to the belly, followed by a warm poultice, have been found to produce much relief. Castor-oil, with Battley's sedative solution, is also given as in other cases. Clysters of this oil may be resorted to when the stomach is too irritable to retain medicine; and in all cases a pint of warm gruel injected into the rectum greatly soothes the patient.

Mr. Williams states that, according to his experience, no relief is obtained unless the patient is kept under the influence of opium for a few hours, before giving purgatives and clysters; that while

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[6] Dr. Garrod, Medico-Chirurgical Transactions, 1854, 36; J. W. Begbie, Edinburgh Medical Journal, 1862; and Charcot, New Syd. Soc. Year-Book, 1864.

[7] Braunal, Retrospect of Medicine, 1867-8.

[8] New Syd. Soc. Year-Book, 1864, p. 167.

[9] Trousseau, Journ. de Chirurgie et de Médecine Pratique, 1862, 33. p. 153. Fatal case of convulsions ascribed to poisoning by lead, but which my friend Dr. Murchison suspects were due to renal disease.

the spasm lasts the use of purgatives is futile, even clysters of castor-oil being expelled without being soiled by fæcal matter or tainted by fæcal odour; that he begins his treatment by administering a dose of 3 or 4 grains of opium; and that in severe cases he has not seen any soothing effect from the injection of warm gruel into the rectum.

Lead-Palsy.—At Guy's Hospital, drugs are prescribed with a view of promoting the excretion of the poison. But some practitioners have recourse to electricity or galvanism, friction and shampooing, or support the wrist by splints in order to relieve the extensor muscles of the weight of the dropped hand. Dr. Rees states that he has occasionally tried the use of splints for this purpose, but not with the benefit that might have been anticipated from the reports of other practitioners in its favour; and, *à priori*, this treatment would appear to be contra-indicated, as tending to prevent the exercise of the affected muscles, and consequently, to promote their further atrophy. Andral entertained a high opinion of strychnine given internally in minute doses in lead-palsy; but experience generally does not seem to have confirmed that opinion; and the administration of such a powerful drug as strychnine is not to be recommended without indisputable proof of its efficacy.

With a view to the elimination of the lead from the kidneys in chronic cases Dr. Rees states that the following treatment has been found advantageous. Iodide of potassium has been given in doses of from 5 to 10 grains twice or thrice daily. Soon after the commencement of such treatment, lead has been detected in the urine. My friend Dr. Sibson, also bears testimony, from his own experience, to the highly satisfactory effect of the iodide upon painters labouring under Lead-Colic. Hot water or hot-air baths have been also employed at Guy's hospital. Dr. Rees has tried both methods, but prefers that of the iodide of potassium, alleging as the reason that the kidney is a more active excretory than the skin. Sulphur-baths, containing 4 ozs. of sulphide of potassium to 30 gallons of hot water, were prescribed by the late Dr. Todd, whereby the patient is stated to have been superficially blackened, owing, it was inferred, to the formation of sulphide of lead in the skin. The same method was adopted by Dr. Guenneau de Mussy in his treatment of the members of the Orleans family, who had been poisoned by drinking water contaminated with lead at Claremont. This treatment seems to be founded on the notion that sulphide of lead is either completely innocuous, or much less so than the compound of lead by which the system is permeated in cases of poisoning by this metal. Assuming sulphide of lead to be harmless, it is fair to infer that this must be due to its insolubility and its undecomposability in the body; but in that case, it may be asked, why should not a patient, who has been poisoned by lead and blackened by a sulphur-bath, remain so as permanently as one who has been blackened by the long-continued internal exhibition of nitrate of silver?

Preventive measures.—This is a subject which imperatively demands the consideration of employers who carry on operations connected

with lead in any form, but which, until a comparatively recent period, has been grievously neglected.[1] A very large number of men and women have been poisoned by lead at smelting and other works (continental as well as British), especially those devoted to the manufacture of white-lead; and have perished prematurely after years of a miserable existence unworthy of the name of life. In many cases the lot of these hapless victims has been inevitable, the only alternatives being to earn their daily bread by honest labour at the risk of health and life, to starve, or to subsist on public charity. The time has passed when manufacturers were allowed to do as they pleased in their establishments with respect to sanitary provisions; and the tendency of our modern legislation is more and more to interfere with a view to promote the health and personal comfort of the labouring classes, who are in large proportion unable to protect themselves. Owners of insalubrious works would do well to consider this and be wise in time. Capital is entitled to an adequate return for its investment, but not at the sacrifice of the health and life of artizans, and the deterioration of their offspring, especially when it is practicable, as in many cases it undoubtedly is, easily to prevent those evils. Moreover, there is good reason for believing that, even in a pecuniary point of view, it will be found highly advantageous to maintain the producers of capital in health, vigour, and contentment, in order that they may render the most efficient service.

With respect to poisoning by lead, every effort should be made to prevent the inhalation of lead-smoke or of air impregnated with plumbiferous dust; and by the adoption of obvious contrivances for efficient ventilation it is certain that this object may be, and in some well-regulated works has been, to a great extent satisfactorily accomplished. It is desirable that everything should be done, as far as practicable, to avert the interference of Parliament and the annoyance of inquisitorial State inspection, with a charge upon the national funds for the salaries of inspectors. At present we have enough of such charges, which in many cases would never have been needed if manufacturers and others had been duly influenced by feelings of humanity.

Rigid attention to personal cleanliness should be enjoined by managers upon their workpeople. Opportunities and time for proper

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[1] Pliny, however, states that in his day preventive measures were adopted by the workers in minium. The passage containing this statement is as follows:—"Qui minium in officinis poliunt faciem laxis vesicis inligant, ne in respirando pernicialem pulverem trahant et tamen ut per illas spectent" (Lib. xxxiii. cap. vii. sect. 39, Sillig's ed.). (They who polish (prepare?) minium in workshops tie up their faces in loose bags, lest in respiring they inhale the pernicious dust, yet so that they may see through them.) The verb "poliunt" probably means the grinding and sifting of the pigment. It is also applied to the winnowing of corn. Pliny uses the word minium for cinnabar as well as red-lead; and in the passage above quoted it is not clear to which he refers. But in either case it appears that the Roman workmen were careful to protect their health by the adoption of means to prevent their inhaling poisonous dust.

ablution should be afforded. Every precaution should be taken to prevent the food and drink of the employed from becoming contaminated with lead; and in order to this, the taking of meals in parts of the works where operations dealing with lead are carried on should be strictly prohibited, and suitable places for that purpose be provided. It has been recommended that the clothes should be changed on entering and before quitting the works, and that during the hours of labour stout linen clothing should be worn instead of woollen; but if expedients for efficient ventilation be introduced, this somewhat troublesome operation of changing garments would probably not be necessary.

But there is another side of the question, which, in justice to employers, ought to be stated; and that relates to the extreme carelessness of the employed and their habitual disregard of the most simple and obvious sanitary precautions. On this subject I have pleasure in inserting the following remarks from an experienced manager of English lead-smelting and other works connected with lead, who I know is a very humane man:—"I have seen a great deal of Lead-smelting Works, and I never saw any sickness which did not arise from attempts to condense the smoke, and I have witnessed much from such attempts. Bad draught is very deleterious to the workman's health, because in that case smoke escapes during puffs of wind. With a good draught, I consider lead-smelting, desilverizing, and even red-lead making, as healthy as any ordinary occupation. The really unhealthy work is the packing of red- and white-lead. It seems easy to suggest remedies, but workmen will not take care, will not permit currents of air, will not do anything except what is easiest for the time being. It grieves me much to see their utter carelessness, the reckless manner, for instance, in which they sweep a floor; for they will not even take the trouble to water it previously, and if you do it for them they only laugh. Education, it is said, will cure all this, but I doubt it." In further illustration, I may mention that at one large white-lead manufactory, baths have been erected for the workpeople, but they will not use them; and it is certainly true, as every one knows who has been accustomed to hospital practice, that many artizans seem to labour under chronic hydrophobia not of canine origin.

Drinks acidulated with sulphuric acid, such as lemonade and treacle-beer, have been strongly recommended, and adopted, it has been asserted, with highly satisfactory results. The latter beverage was tried in 1841 at the British White-Lead Works near Birmingham, where I was a frequent visitor; and, according to the late Mr. Benson, the manager, lead-colic, which had previously prevailed to a distressing extent, soon began to diminish in frequency after the use of this beverage, and during a period of fifteen months not a single instance of the malady occurred. M. Peligot has recently announced, on the authority of the director of some extensive works in France connected with lead, that the introduction of the free use of milk as a beverage by the men has resulted in the disappearance of lead-colic, which had

been previously common.[4] However beneficial the adoption of prophylactics of this kind may be, nothing should divert attention from the one thing needful, the prevention of the introduction of the poison into the system.

I will conclude with the words of an old author. "But as great Profit arises to Princes and Merchants from Mines, and as the Use of Metals is highly necessary to almost all Arts, we are therefore bound in duty to preserve the lives of these workmen by investigating their Diseases, and proposing Cautions and Remedies for the Removal of them."[5]

Poisoning of Animals by Lead.

It is stated by Sir Thomas Watson, that dogs, cats, and rats, which inhabit buildings, wherein lead is much used or prepared, are known to be attacked both with colic and with palsy. An interesting communication on the poisoning of horses and cows by lead, was made in 1852, by my deceased friend, Dr. George Wilson, to the Royal Society of Edinburgh; and the main facts recorded therein are as follow. In the year previous he made a series of analyses in connection with the death of thirteen horses, which, besides several cows, were believed to have been poisoned by compounds of lead, transferred by the atmosphere or by water to fields in which they pastured. He found the herbage of those fields to be notably impregnated with carbonate of lead, and conceived it to be highly probable, that all the deaths had been caused by this poison. The proprietors of lead-works in the vicinity seemed to have arrived at the same conclusion; for, after a little delay, they declined going into a court of law, and compensated the owners of the dead horses. Eleven of the cases occurred in Derbyshire, and two in Westmoreland. In the latter, a brood mare and a pony had pastured in a field adjoining the Greenside Lead Mine, which is situated near Patterdale, among the hills surrounding the head of Ullswater Lake. A stream, proceeding from the mine, and employed in washing the ore, ran through this field, at which the horses were accustomed to drink. The water, taken from the stream on a day when the ore was being dressed, contained a large quantity of carbonate of lead, chiefly in the form of sediment, but also to some extent in suspension. This, however, was not the only source whence lead entered the bodies of the animals. During a heavy winter flood, the stream above mentioned had been negligently allowed to burst its barriers and suddenly to overflow the neighbouring fields, which, it is stated, became literally covered with a thick coat of the *scum from the mines*, so that persons were set—by the Company, it was understood—to scrape it off the grass. A portion of grass and soil taken from the field referred to some months after the overflow, was examined by Dr. Wilson. The blades and roots were operated on separately, and

[4] British Medical Journal, June 11, 1870, p. 608.

[5] Health Preserved. By Bern. Ramazini, M.D., Chief Professor of Physick at Padua. Translated by R. James, M.D. 2nd ed. London, 1750. p. 38.

both yielded a large quantity of lead, which, he supposed, probably existed in the state of carbonate. Beans grown in Edinburgh in the soil which was sent along with the grass, contained lead. It was clearly ascertained that the mare and pony had during six weeks or more daily swallowed carbonate of lead in their food and drink. At the end of this period, both animals had become so much emaciated, and otherwise out of condition, that they were removed to a field at some miles' distance, free from impregnation with lead. They survived the change a fortnight, and died rather suddenly within a short time of each other. No lead was detected in the contents of the stomach and cœcum of the pony, but the substance of those viscera yielded a small, though manifest, quantity of the metal. The mare had been buried, but was exhumed, and portions of the lungs, heart, large intestines and their contents, stomach and duodenum, spleen and liver, and one kidney, were subjected to analysis. Gaultier de Claubry's method of destroying the organic matter by digestion with nitro-hydrochloric acid was adopted in the examination; and the tests applied were sulphuretted hydrogen, sulphuric acid, iodide of potassium, and bichromate of potash; all the substances above mentioned gave conclusive indications of the presence of lead, which, however, was too small in amount to admit of comparative quantitative determination by the balance. But as far as it was possible to make a comparative estimation from the quantity and colour of the precipitates, the lead was found to exist in relatively less proportion in the following order, spleen, liver, lungs, kidney, and intestines. The spleen seems to have contained a considerable quantity of lead, even notably more than the liver; and the intestines only traces. Dr. Wilson examined the Derbyshire cases, but did not succeed in finding a trace of lead.

The inferences, which the preceding data suggested to Dr. Wilson, are as follow: 1st. That as all the organs subjected to analysis were found to contain lead, it is probable that, if additional parts of the animal had been analysed, they would have been found to contain it also, so that, in cases of slow poisoning, we may safely infer that a metal like lead comes to be diffused through the entire body, and exerts its poisonous action, though in unequal degree, on every organ; and 2dly. That lead having once entered the body in this way, leaves it again very slowly, so that long after an animal has ceased to receive lead in its food and drink, we may expect to find the metal in its tissues; and the restoration of health must always be a protracted process.

The following interesting letter on the subject of the poisoning of cows by lead, which I have slightly abridged, was communicated to 'The Times,' Aug. 1, 1864, by Mr. Tuson, Professor of Chemistry in the Royal Veterinary College:—"In May last three cows, the property of Mr. Mullins, of Rugby, died, after exhibiting symptoms which could not be referred by Mr. Watson, the veterinary surgeon consulted, to any disease with which he was acquainted. On making a *post mortem* examination of the cows, fragments of lead were found in their alimentary canals, especially in the reticuli, or paunches. It

was then remembered that the whole of the cows affected, although they had from November, 1863, up to the period of their death in May last been pastured at a distance from the butts of the Rugby Rifle Volunteer Corps, had prior to November, 1863, been kept in a field immediately adjoining those butts. This field was carefully examined by Mr. Watson, and among the herbage he discovered fragments of lead, which corresponded in every way with those found in the stomachs of the cows. Now, the lead here referred to is that which had been scattered from the targets consequent upon the impact of bullets, and is called "bullet-spray." Some of this spray had been evidently picked up by the cows while feeding, it remained in their stomachs several months, where during that time it slowly, but continuously, underwent solution, and subsequent absorption into the system, and so, doubtless, poisoned the animals in question.

"Since the death of the three cows the owner has lost two more, under precisely the same circumstances as those already related. The viscera of one of the cows which died last was sent to me for analysis, and I was enabled to demonstrate the presence of lead not only in the coats of the stomach and intestines, and in their contents, but likewise in the liver and kidney; thus proving the passage of the poisonous metal into the circulation. I also had an opportunity of examining the bullet-spray, which enabled me to ascertain that most of it was incrusted with a pale drab-coloured substance, composed chiefly of carbonate of lead—a highly poisonous plumbic compound. It was this carbonate of lead which, I believe, more immediately caused the death of the cows."

APPENDIX.

Sulphide of Iron heated with Litharge.

(See p. 31.)

In the preceding volume of this work, on the Metallurgy of Iron and Steel, the results which Berthier obtained in his experiments concerning the oxidizing action of litharge on proto-sulphide of iron, have been recorded (p. 36). When considerably more litharge is present than suffices for the conversion of the sulphur into sulphurous acid and the iron into oxide, soft metallic lead is separated; but with sensibly less litharge, lead containing sulphide of lead is formed. The degree of oxidation of the iron was not satisfactorily ascertained.

Reduction of Silicate of Lead by Iron.

(See p. 34.)

Silicate of lead was prepared according to the formula $2PbO,SiO^3$, by heating a mixture of red-lead (Pb^3O^4) and fine sand in a vessel of platinum, during 2½ hours in a muffle, at the temperature of dull redness, so as to *frit* and not melt the mass. The temperature was afterwards raised sufficiently to cause perfect fusion, and kept at that degree during about half an hour. The mixture operated upon consisted of 11,415 grains of red-lead and 2250 grains of sand. While the product was molten its colour was very dark, and might almost be described as black; but when solid it was vitreous, transparent, and of a light amber-colour. It was poured out, and after solidification the whole of it was reduced to powder, in order to secure uniformity of composition throughout. Of this powder 3000 grains were heated in a wrought-iron crucible, placed in a clay crucible, and covered so as to protect the contents from the reducing action of the fuel and furnace gases. Fusion took place at the temperature of dull redness, but no reduction of the silicate was perceived until it rose to full redness, when globules of lead began to separate, and continued to do so for three-quarters of an hour. During the process the heat was gradually raised, in order to produce the requisite fluidity in proportion as the oxide of iron formed was augmented. After the lapse of an hour the product was poured out at the temperature of strong redness, and was found to be composed as follows:—

Soft lead	2212 grains
Black, largely-crystalline slag	1418 do.

Of this slag 1115 grains were re-melted and kept fused during an hour in the same wrought-iron crucible as previously used. In this operation lead to the amount of 13 grains was separated, which corresponds to 16·5 grains in the

whole of the original slag. The slag produced in the second fusion was found to have the following composition per cent:—

			Oxygen.
Protoxide of iron	68·25	.....	15·15
Sesquioxide of iron	2·57	.....	0·77
Protoxide of lead (= 0·64 of lead)	0·82		
Silica	28·36	.....	14·73
	100·00		

Hence this slag may be regarded as essentially tribasic silicate of protoxide of iron, mixed with a little sesquioxide or probably magnetic oxide of iron and silicate of lead. The results of the foregoing experiment may be tabulated as under:—

	Per cent.
Lead present in the silicate of the formula $2PbO,SiO^3$	77·24
Lead obtained in the first fusion	73·73
Lead obtained in the second fusion	0·55
Lead left in the slag from the second fusion	0·10
Lead lost by volatilization and otherwise	2·66
	77·24

SULPHIDE OF LEAD HEATED WITH OXIDE OF COPPER.

(P. 54, before *Sulphide of lead heated with the fixed alkalies*, &c.)

In the first volume of this work the results of experiments made by Smith in my Laboratory, on the action of protoxide of copper on sulphide of lead, have been recorded; and I now insert the results obtained by Berthier, in similar experiments with dioxide as well as protoxide of copper. (Tr. des Essais, 2, p. 673.)

	Ratio of mixture.	Quantities operated upon in grammes. Sulphide of lead.	Dioxide of copper.
I.	PbS : $2Cu^2O$	29·9	35·6
			Protoxide of copper.
II.	PbS : CuO	29·9	9·9
III.	PbS : 2CuO	29·9	19·8
IV.	PbS : 3CuO	29·9	29·7

I. The products were 21 grms. of dry copper (*cuivre rouge*), 9 grms. of regulus—chiefly, and perhaps entirely, composed of disulphide of copper—and a red slag, in which nearly the whole of the lead is present in the state of oxide.

II. The products were 20 grms. of double sulphide of copper and lead, and a glassy opaque slag, of a fine red colour, composed of oxide of lead and dioxide of copper.

III. The products were a double sulphide, similar to the preceding, but in much smaller quantity, and enveloped in a glassy, red, very brilliant (*très éclatante*) slag. By heating very strongly, a button of pure copper, weighing 11·5 grms., was obtained along with a glassy red slag.

IV. The products were a button of perfectly pure dry copper, weighing 17 grms., and a red slag.

Sulphide of Lead heated with Tin.

(See p. 59.)

The upper layer has been analysed by Ward in my Laboratory, and found to be composed as follows:—

	Per cent.		Ratio of equivalents.	
Tin	48·67	.....	0·825	2
Lead	34·44	.....	0·332	1
Sulphur	16·86	.....	1·050	3
	99·97			

In preparing the material for analysis the whole of the upper layer was reduced to powder and sifted, in order to separate, as far as practicable, metallic particles with which it was found to be intermixed. The composition of this upper layer is approximately represented by the formula, PbS + 2SnS. The reaction may be indicated by the equation

$$3PbS + Sn^6 = PbS + 2SnS + Pb^2 + Sn^4$$

Composition of the Crust formed on the exterior of a Lead-pipe.

(See p. 67.)

A lead-pipe has recently been taken up from a flooring of concrete, in what was formerly the Carnivora House at the Zoological Gardens, Regent's Park, where it had been imbedded during more than 30 years. It was thickly coated externally with compact amorphous matter in successive layers, which was yellowish near the surface, and internally was in some places blueish-grey and in others greenish. It had become much contracted by the pressure resulting from the formation of the encrusting matter. It is probable that the urine of the animals had found its way to the exterior of the pipe. The crust has been analysed by Ward in my Laboratory, and found to have the following composition (1870).

Protoxide of lead	89·80
Peroxide of tin with traces of antimony	1·28
Water	5·36
Carbonic acid	0·96
Nitric acid / Nitrous acid	2·60
	100·00

The lead and tin estimated in the metallic state amount to 83·36% and 1·02% respectively.

Additional Results obtained in the Harz in Cordurié's Process.

Extracted from the Zeitschrift für das Berg-, Hütten- u. Salinen-Wesen in dem preussischen Staate. 1870. 18. p. 46.

(See p. 174.)

Wedding and Bräuning have recently published the following statement of the result of the working of the zinc and steam desilverizing process at Lau-

tenthal, as applied to the silver-lead produced in the Upper Harz Lead Works. The quantity of lead treated was 22,053 centners.

	Silver.	Lead.		Percentage of total quantity.	
				Silver.	Lead.
MATERIALS TREATED.	lbs.	Ctrs.	lbs.		
22,053 ctrs. of furnace-lead (Werkblei), containing	3,168·31	22,021	32	100·000	100·000
YIELD.					
1. Merchantable products:					
Blicksilber, 3,525·51 lbs. containing of fine silver	3,243·47	..		102·372	..
Refined Harz lead	..	18,803	88	..	85·389
Good pig-lead	..	1,907	63	..	8·662
Hard lead	..	489	58	..	2·223
Oxides of lead and zinc, free from silver	..	55	20	..	0·250
Litharge, 64 ctrs.	..	58	88	..	0·267
Total of merchantable products ...	3,243·47	21,315	17	102·372	96·791
2. Intermediate products not merchantable:					
167 ctrs. dross from liquation of the pig-lead, containing by assay 96% of lead	..	160	32	..	..
69 ctrs. dross from liquation of hard lead, containing by assay 86% of lead	..	59	34	..	..
94 ctrs. hearth-bottoms, containing by assay 68% of lead	..	63	92	..	..
111 ctrs. rich litharge, containing by assay 90% of lead	..	99	90	..	..
11 ctrs. Abstrich, containing by assay 80% of lead	..	8	80	..	..
		392	28	..	1·781
Total of silver and lead accounted for	3,243·47	21,707	45	102·372	98·572
Difference corresponding to apparent loss	−75·16	313	87	−2·372	1·428

The apparent excess of 2·372% of silver is accounted for by the loss in the assay by cupellation, for which no allowance is made: assuming this to be about 3%, the real loss of silver will be 0·628%.

That there is an actual gain by the application of the steam process is proved by the fact that the yield when the blast-furnace was used for the treatment of the argentiferous zinc always showed a small deficiency on the assays. The loss of lead is said to be no more than may be accounted for in the cupellation of the enriched lead and reduction of the litharge, so that no part of it is chargeable in reality to the desilverizing process.

The refined lead is that produced directly from the desilverizing pots by the process of refining by steam; the so-called good pig-lead is a second quality, containing traces of copper, and is obtained partly from the shots of metals recovered from the mixed oxides by washing, and partly from the reduction of the dross of the refined lead; the hard lead is obtained from the reduction of Abstrich, and is treated with steam in order to remove traces of zinc and copper.

The mixed oxides, containing from 60% to 67% of oxide of zinc, and from 33% to 40% of protoxide of lead, are sold for conversion into paint.

Recent experiments have shown that the refined Harz lead contains traces of bismuth, which were formerly regarded as copper. It may therefore be inferred that bismuth cannot be removed from lead by zinc in the same manner as is the case with copper, gold, and silver.

It has also been found that when zinc is added in quantity less than sufficient for complete desilverization, or in the proportion of not more than 40 lbs. to a charge of 12½ tons of lead, the greater part of the copper, together with the whole of the gold contained in the furnace-lead, is removed in the first skimmings. In this way small quantities of gold may be concentrated in the first portions of the enriched lead, which on cupellation yield silver containing from 0·12 to 0·20 quint (1 quint=5 grammes) of gold per lb., an amount that may be profitably separated by the process of parting.

On Lead-Smelting in England in the 17th Century.[1]

(See p. 216.)

The following account of the method of lead-smelting formerly practised in England, is the most interesting that I have met with:—

"There is *Sparr* and *Caulk* [sulphate of baryta, usually spelt cawk] about the Ore; and another substance, which they call the *Crootes*, which is a mealy white stone, marked with Ore, and soft. The *Sparr* is white, transparent, and britle like Glass. The *Caulk*, white and heavy, heavier than any stone. The *Vein* lies between the Coats, and is of different breadths. It breakes off sometimes abruptly in an Earth, they call a *Deading Bed*, and after a fathom or two may come again, keeping the same point. It terminates sometimes in a dead Earth Clayie, without *Croot* or *Sparr*; sometimes in a Rock called a *Fore-stone*.

"There is much difference in the goodness of the Ore. The cleerest and heaviest, best. 36 hundred of Ore may yield a Tun of Lead. Some small eyes of other mixtures, Brass, &c.

"They beat the Ore with an Iron flat piece; cleanse it in Water from the dirt; sift it through a Wire-sive. The Ore tends to the bottom, and the Refuse lies at top. And these are the Preparations, they make use of, before 'tis fit for fusion. Then they have a Hearth about 5 foot high, set upon Timber, to be turn'd as a Wind-mill, to avoid the inconvenience of smoak upon a shifting Wind. The Hearth contains half a bushel of Ore and Coal, with bellowes on the top. The Charcoale is put upon the Hearth, where the Ore is; laying dry Gads upon the top, which they call their White coales. There is a sink upon the side of the Hearth, into which the Lead runs, that holds about an hundred and an half. Then it is cast into Sand, and runs into those *Sowes* (as they call them) which they sell. They have a barr, to stir the Fire; a Shovel, to throw it up; and a Ladle heated red-hot, to cast out the Mettal.

"Once melting is enough. The good melts best, and the best, first. There is sometimes half odds in the goodness. The best is distinguisht by its weight.

"There is a *flight* in the smoak, which falling upon the Grass, poysons those Cattel that eat of it. They find the taste of it upon their lips to be sweet, when the smoak chances to fly in their Faces. Brought home, and laid in their houses, it kills Rats and Mice. If this flight mix with the Water, in which the Oar is wash't, and be carried away into a streame, it hath poisoned such Cattel, as have

[1] Mr. Joseph Glanvil on the Mendip Mines, Philosophical Transactions, 1668, 3, p. 770.

drunk of it after a current of 3 Miles. What of this *flight* falls upon the sand, they gather up to melt in a Slagg-hearth, and make Shot and Sheet-lead of it.

"They sometimes find *Slaggs*, 3, 4, or 5 foot under ground, but such as they judge cast aside heretofore."

COMPOSITION OF THE REGULUS OBTAINED IN SMELTING AUSTRALIAN LEAD ORE.

(See p. 431.)

This regulus has been analysed by Smith in my Laboratory, and found to have the following composition:—

COMPOSITION OF REGULUS.

Iron	51·61
Lead	13·50
Copper	4·99
Silver	0·077*
Sulphur	27·80
Sand	0·10
	98·077

* 25 ozs. 3 dwts. 2 grs. per ton.

Arsenic was sought for, but not detected. The yield of lead by dry assay was 12·7%. The composition of this regulus may be approximately represented by the following formula:—

$$15\,(4FeS + Fe^2S) + PbS + Cu^2S$$

TABLE FOR COMPUTING FROM THE PERCENTAGE OF SILVER THE TROY WEIGHT OF SILVER PER STATUTE TON.

Per cent.	Per ton.				Per cent.	Per ton.			
	Grains.	ozs.	dwts.	grs.		Grains.	ozs.	dwts.	grs.
0·0001	15·68	0	0	15·68	0·06	9,408·0	19	12	0·0
0·0002	31·36	0	1	7·36	0·07	10,976·0	22	17	8·0
0·0003	47·04	0	1	23·04	0·08	12,544·0	26	2	16·0
0·0004	62·72	0	2	14·72	0·09	14,112·0	29	8	0·0
0·0005	78·40	0	3	6·40	0·1	15,680·0	32	13	8·0
0·0006	94·08	0	3	22·08	0·2	31,360·0	65	6	16·0
0·0007	109·76	0	4	13·76	0·3	47,040·0	98	0	0·0
0·0008	125·44	0	5	5·44	0·4	62,720·0	130	13	8·0
0·0009	141·12	0	5	21·12	0·5	78,400·0	163	6	16·0
0·001	156·8	0	6	12·8	0·6	94,080·0	196	0	0·0
0·002	313·6	0	13	1·6	0·7	109,760·0	228	13	8·0
0·003	470·4	0	19	14·4	0·8	125,440·0	261	6	16·0
0·004	627·2	1	6	3·2	0·9	141,120·0	294	0	0·0
0·005	784·0	1	12	16·0	1·0	156,800·0	326	13	8·0
0·006	940·8	1	19	4·8	2·0	313,600·0	653	6	16·0
0·007	1,097·6	2	5	17·6	3·0	470,400·0	980	0	0·0
0·008	1,254·4	2	12	6·4	4·0	627,200·0	1306	13	8·0
0·009	1,411·2	2	18	19·2	5·0	784,000·0	1633	6	16·0
0·01	1,568·0	3	5	8·0	6·0	940,800·0	1960	0	0·0
0·02	3,136·0	6	10	16·0	7·0	1,097,600·0	2286	13	8·0
0·03	4,704·0	9	16	0·0	8·0	1,254,400·0	2613	6	16·0
0·04	6,272·0	13	1	8·0	9·0	1,411,200·0	2940	0	0·0
0·05	7,840·0	16	6	16·0	10·0	1,568,000·0	3266	13	8·0

INDEX.

"ABSTRICH."

A.

"ABSTRICH," 173–4, 194–5, 199, 300, 478–9.
"Abtreiben," 185.
"Abzug," 91–2, 173–4, 193–5, 198.
Acetate of ammonia and sulphate of lead, 40.
Acetic acid, its action on lead, 10; on sulphate of lead, 40.
——, for dissolving oxide of lead from cupels, 464.
Acid, antimonious, with protoxide of lead, 18.
——, arsenic, with protoxide of lead, 18.
——, arsenious, with protoxide of lead, 18.
——, hydrochloric. *See* Hydrochloric acid.
——, nitric, action of, on lead, 10.
——, plumbic, 24.
——, protoxide of lead as an, 16.
——, stannic, with protoxide of lead, 17.
——, titanic, with protoxide of lead, 18.
Acid-drinks, use of, for lead-workers, 529.
Acids, action of, on lead, 10–88.
Act of Parliament for manufacture of milled lead, 501.
Action of acids on lead, 10–88.
—— of atmosphere on lead and copper, 92.
—— of bicarbonate of lime on sulphate of lead, 40.
—— of boiled water on monocarbonate of lead, 70.
—— of boiling water upon lead, 10.
—— of cadmium on nitrate of lead, 11.
—— of carbonate of ammonia on sulphate of lead, 40.
—— of distilled water with air on lead, 68.
—— of fixed alkaline carbonates on sulphate of lead, 40.
—— of hyposulphite of soda on sulphate of lead, 42.
—— of iron on sulphide of lead, 56.
—— of lime in Flintshire furnace, 236.
——, oxidizing, of litharge, 18.
—— of pressure on finely-divided lead, 9.
—— of vapour of water on sulphide of lead, 50, 51.
—— of water on galena, 37, 51; on protoxide of lead, 15; on sulphate of lead, 40.
—— of zinc on nitrate of lead, 11.
Actynolite with galena, 95.
Adhesive property of lead, 9; with tin, 9.

AMERICAN.

Adkins, Mr., his red-lead ovens, 509; concretionary deposit on, 519.
——, lead for making red-lead used by, 516.
Adra, Carthagena furnace at, 423, 429; Flintshire furnace at, 244; "Horno reverbero" at, 247, 254.
African furnaces, resemblance of Carthagena furnaces to, 421.
Agricola on refining, 209, 212.
Air-furnaces, 213–215, 421.
Air-reduction process, 219, 220, 491.
Ajmír, lead-smelting at, 293.
Albertville, lead-smelting at, 244.
Alderley Edge, lead in copper-bearing sandstone of, 352.
Alguira, lead-smelting at, 255.
Alkalies (fixed), or their carbonates, with nitre and sulphide of lead, 53; with carbon and sulphide of lead, 54.
Alkaline carbonates (fixed), and sulphate of lead, 40, 42.
—— and earthy sulphates, with sulphate of lead, 43.
Alloy for lead-shot, 71.
—— of lead and antimony, 86; potassium, 88; sodium, 90; copper, 91; manganese, 93.
—— of antimony, copper, and nickel from smelting-furnace, 378.
—— from liquation of hard lead, 467.
Almeria, lead-smelting at, 255.
Alport, Flintshire furnace at, 240; Spanish slag-hearth at, 419.
—— "linnets," 433, 434.
——, lead-fume condensing at, 438.
"Alquifoux," 94.
Alston (Eggleston Mill), lead-fume condensing at, 447.
Alston Moor, lead-fume from, 454.
Altenau, marl, &c. for furnace-bed at, 188.
——, lead-smelting with iron at, 369.
——, roasting lead-regulus at, 382, 383.
——, Rachette furnace at, 385.
——, treatment of copper-slags at, 388–390.
——, slags from Schlieg-smelting at, 394.
——, composition of lead from, 493, 494.
Alumina, lime, and protoxide of lead, silicate of, 36.
Amalgam, native, at Sala, 296.
America, lead-smelting in, 289.
American ore-hearth, 289; at Bleiberg 292; at Przibram, 293.

AMMONIA.

Ammonia, acetate of, its action on sulphate of lead, 40.
——, carbonate of, its action on sulphate of lead, 40.
Ammonium, chloride of, and sulphide of lead, 66.
Analyses—Optical glass, 35.
——, sulphates of lead, 41, 42.
——, roasted sulphides of lead and iron, 47.
——, regulus from sulphide of lead and silicate of iron, 59; of slag, 59.
——, regulus from galena and copper, 61.
—— (partial) of composition of product from sulphide of lead and chloride of sodium, 66.
——, product from sulphide of lead and chloride of ammonium, 66.
——, product from galena and hydrochloric acid, 82.
——, brown crust from oxidation of lead and copper, 93.
——, galena with manganese, 95.
——, bournonite, 98.
——, dezincified lead, 162.
——, lead from treatment by chloride of sodium, 161.
——, lead in dezincification, 163.
——, partly dezincified lead, 165.
——, lead softened in cupellation-furnace, 166.
——, refined lead, 174.
——, lead decopperized by zinc, 176.
——, marl, clay-slate, &c., for furnace-bed, 188.
——, "Abzug," 198.
——, "Abstrich," 199–200.
——, lead from which "Abstrich" was derived, 200.
——, bismuthic litharge, 202.
——, dolomite for cupelling hearth-bed, 206.
——, ore for Flintshire furnace, 234.
——, products from Flintshire furnace, 239.
——, slags from Lea Smelting Works, 241.
——, grey-slag, Tarnowitz, 242.
——, "laja" in Spanish furnace, 247.
——, Bleiberg lead, 267; grey-slag, 268.
——, slag from American ore-hearth at Bleiberg, 292.
——, roasted ore, Freiberg, 308.
——, blast-furnace lead, Freiberg, 312; regulus, 313; slags, 314.
——, seven-twyer furnace slag, Freiberg, 316.
——, copper-regulus, Freiberg, 317; slag, 317; regulus from slag, 318.
——, reverberatory furnace regulus, Freiberg, 324; slag, 324; of slags from slag- and ore-smelting with carbon, 325.
——, accessory product from Freiberg process, 326; of lead-grey furnace-bed product, 327.
——, enriched regulus, Freiberg, 334.
——, roasted and agglomerated ore, Pontgibaud, 341; of roasted but unagglomerated ore, 342.

ANDREASBERG.

Analyses—Regulus, Pontgibaud, 343; of slags, 344.
——, slag, at La Pise, 349.
——, slagged ore, at Münsterbusch, 356; of slag from the slagged ore, 356.
——, ores used in iron-reduction process, Friedrichshütte, 358.
——, Tarnowitz lead, 368.
——, Clausthal and Zellerfeld lead-ores, 369.
——, Upper Harz furnace-lead, 372.
——, lead-regulus from Andreasberg, 373.
——, lead-regulus from Clausthal, 373; from Lautenthal, 373.
——, lead-speise, 376.
——, crystallized sulphide of lead from Clausthal, 377.
——, crystallized alloy from smelting works, 378.
——, slags from smelting "Schlieg," 379.
——, regulus from smelting lead-regulus, 383; of slags, 383.
——, copper-slag for reduction of galena, 387; of cast-iron from copper-slag, 388; of pig-iron, 390.
——, lead-slags from Sophienhütte, 390, 391.
——, lead-regulus from Rachette furnace and Schliegofen, 393.
——, slags from Schlieg-smelting in Rachette furnace, 394; in one-twyer furnace, 394.
——, Przibram lead-ores, 399; Przibram blende, 399.
——, roasted lead-ore, Przibram, 406; lead-regulus, 407, 408; slag, 408, 409.
——, black-slag from Spanish slag-hearth, 421.
——, Australian lead-ore, 430; regulus from, 538.
——, lead-fume, 451–455.
——, Derbyshire slag-lead used in Baker's softening process, 465; of lead from dross in softening, 466, 467.
——, alloy from liquation of hard lead, 468; of liquated and poled lead, 470.
——, Freiberg litharge slags, 476.
——, Clausthal clay, 478.
——, different kinds of lead at Vienna, 493; at Clausthal, 494.
——, Ballycorus red-lead, 516.
——, German and Spanish lead, 495.
——, concretionary matter from drossing-oven, 520.
——, slag from reduction of silicate of lead by iron, 534.
——, upper layer from sulphide of lead heated with tin, 535.
——, crust formed on lead-pipe, 535.
See Composition.
Andalusia, lead-smelting in, 255.
Andes, lead-smelting in the, 275.
Andral, his use of strychnine for lead-palsy, 527.
Andreasberg slag-lead, 174.

ANDREASBERG.

Andreasberg lead-ores, 369.
——, lead-smelting at, 370.
——, lead-regulus from, 373.
——, lead-speise at, 376.
—— furnaces, arsenical compounds from, 378.
——, regulus-smelting at, 383.
Anglesite, 98.
Animals, poisoning of, by lead, 530.
Anthon on oxychloride of lead, 80.
Anthracite, galena with, 95.
Antimoniate of protoxide of lead, 86.
Antimonious acid with protoxide of lead, 18.
Antimony, oxide of, with protoxide of lead, 18.
—— and litharge, 19, 201; and sulphide of lead, 62.
——, sulphide of, with sulphide of lead, 38; with lead, 62; in lead-ore, 485.
—— and lead, 86; sulphides of, 98; crystallization of, 146.
—— in galena, 95.
——, its influence upon assay with fluxes in iron crucible, 119.
——, its effect in Pattinson's process, 138, 147.
——, elimination of, in cupellation, 202.
——, copper, and nickel alloy from smelting-furnace, 378.
—— in dross from lead-softening, 466.
—— used with lead for gas-pipes, 507.
——, its oxidizing effect on lead, 517.
Aragonite with galena, 95.
Argol, red and white, in assay of lead-ore, 106.
Arqueros, pyromorphite from, 77.
Arrayañez, lead-smelting at, 247, 252.
Arseniate of lead, 100; native arseniate, 74.
——, protoxide of lead, 73; with chloride of lead, 74.
—— of cobalt with galena, 95.
Arsenic and litharge, 19.
——, sulphide of, and lead, 63.
—— and lead, 71; crystallization of, 146.
—— in shot, 72; in litharge, 201; in lead-ore, 486.
——, its influence upon assay with fluxes in iron crucible, 119.
——, its effect in Pattinson's process, 138.
Arsenic acid with protoxide of lead, 18.
—— —— in pyromorphite, 100.
Arsenical compounds in Andreasberg furnaces, 378.
Arsenide of lead, 71.
Arsenious acid with protoxide of lead, 18.
Arsenites of protoxide of lead, 73.
Asbach, accidental production of red-lead at, 519.
Assay of galena, use of iron in, 56; in iron crucibles with fluxes, 106; in iron dishes, 108; affected by certain substances, 113–119.
—— of lead-ores, 103; sampling, 103; furnace and implements, 104; fluxes, 106; in earthen crucibles with iron, 110;

BASIC.

in iron crucibles without fluxes, 110; wet assay, 120.
Assay of carbonate and phosphate of lead, 112.
—— of lead at Bleiberg, 270.
Assays of copper- and lead-slags from Lower Harz, 389.
Atmosphere, influence of, on lead, 67; on alloy of lead and copper, 92.
"Atocha," 425.
Atomic weight of lead, 10.
Audouin, M., lead grooved by insects shown by, 521.
Australian lead-ore, 430; regulus from, 538.
Austro-Hungarian Empire, production of lead in, 499.
Avenarius on lead-regulus from Andreasberg, 373.

B.

BABYLON, enamelled brick from, 88.
Bagillt, lead-smelting at, 229, 239.
——, products of smelting galena at, 239.
——, slag from Spanish slag-hearth at, 420.
——, Australian lead-ore at, 430.
——, specimens of lead-fume from, 451.
Baker, Mr., on elimination of metals from lead by crystallization, 144.
—— on concentration of copper in Pattinson's process, 146.
—— on crystallization of lead with antimony, 146; with tin, 146; with arsenic, 146.
—— on decopperization of lead by zinc, 174.
——, his process for softening hard lead, 465.
—— on red-lead manufacture, 512.
—— on lead for making red-lead, 518.
—— on concentration of copper in unoxidized lead, 519.
—— on decopperization of lead, 519.
Balling on lead-regulus, 406.
Ballycorus, red-lead manufacture at, 514.
Banks, Sir J., on a plant peculiar to lead-bearing soil, 215.
Barba on lead-smelting in Peru, 215.
—— on reverberatory furnace with wood fuel, 218.
Barker, Mr. F., his drawings of Spanish slag-hearth, 419; of lead-fume condensing apparatus, 438.
——, Mr. J., his iron crucibles, 108.
Barker and Rose, Messrs., on lead-smelting at Alport, 240.
Baryta, plumbate of, how made, 25.
—— and protoxide of lead, silicate of, 36.
—— and sulphide of lead, 55; with carbon, 55.
——, sulphate of. *See* Sulphate of baryta.
Barytes (sulphate of baryta or "cawk") with galena, 95.
Basic nitrates of protoxide of lead, 85.

Basic silicate of protoxide of iron, lead-smelting with, 384.
Baths of Titus, red-lead in vase from, 509.
Baudrimont on tenacity of lead, 8.
Bauerman, Mr., on "alquifoux," 94.
—— on the lead-ores of Commern, 350.
Beaumont, Mr., flues at smelting-works of, 438.
——, his pig-lead for making white-lead, 508.
Beccher, his use of pit-coal for smelting, 218.
Beck, Dr., on lead and boiling water, 10, 11.
—— on silicates of protoxide of lead, 27, 28; with sulphur, 30; with charcoal, 31; with carbonate of soda and charcoal, and with carbonate of lime and charcoal, 33; with iron, 33; with sesquioxide of iron and charcoal, 34; with soda, 36; with lime, 36.
—— on silicate of lead with protosulphide of iron, 31.
—— on sulphide and silicate of lead, 48.
Beckmann on the word "galena," 94.
Becquerel, E., on electric conductivity of lead, 9.
—— on crystallized protoxide of lead, 14.
—— on peroxide of lead, 24.
Belgium, cost of Pattinson process in, 139.
——, lead-smelting in, 229, 245.
——, production of lead in, 499.
Bell, Mr. I. Lowthian, on oxychloride of lead, 79, 81.
Benson, Mr., on treacle-beer for lead-workmen, 529.
Benson and Gossage, Messrs., white-lead made by, 69.
Beresowsk, galena with gold from, 96.
Berja, lead-smelting at, 247, 254.
Berthier on tenacity of lead, 7.
—— on volatilization of lead, 9.
—— on protoxide of lead with iron-scales, 17; with sesquioxide of iron, 17; manganese, 17; stannic acid, 17; antimonious acid, 18; arsenious acid, 18; arsenic acid, 18.
—— on litharge with selenium, 19; with arsenic, 19; antimony, 19; tin, 20; bismuth, 20; zinc, 21; iron, 21.
—— on silicate of protoxide of lead, 30; with lime, 36; with lime and alumina, 36.
—— on sulphide of lead, 37; with oxide of copper, 534.
—— on sulphate of protoxide of lead, 41.
—— on sulphate of lead with silica, 43; with protoxide of lead, 43; chloride of lead, 43; with alkaline and earthy sulphates, 43; with chloride of sodium or potassium, 43; fluoride of calcium, 44; fluoride of calcium and lime, 44.
—— on sulphide of lead, with carbonate of soda, 53; with fixed alkalies or their carbonates, and nitre, 53; and carbon, 54; black oxide of manganese, 54; lime, 54; sesquioxide of iron, 56; copper, 60; antimony, 62.
Berthier on arseniuretted lead, 71.
—— on arsenites and arseniates of lead, 73.
—— on phosphates of lead, 76.
—— on chloride of lead, and sulphur, 78; and galena, 79.
—— on oxychloride of lead, 81.
—— on lead and manganese, 93.
—— on black colour of "Abstrich," 201.
—— on oxide of lead and bismuth, 202.
—— on galena and lime, 236.
—— on slag from Lea Smelting Works, 241.
—— on adding galena to bath of lead in German cupellation-furnace, 364.
—— on lead-fume, 454, 455.
—— on galena and iron-scales, 483.
—— on china-clay and litharge, 489.
Berzelius on specific gravity of lead, 3.
——, his atomic weight of lead, 10.
—— on lead and oxygen, 10.
—— on dioxide of lead, 11.
—— on reduction of protoxide of lead, 15.
—— on hydrated protoxide of lead, 22.
—— on lead and silicon, 27.
—— on carbide of lead, 67.
—— on lead and arsenic, 71, 73.
—— on chloride and sulphide of lead, 79.
—— on basic nitrate of protoxide of lead, 85
—— on nitrites of protoxide of lead, 86.
Beust, Von, on loss in lead-slag smelting at Freiberg, 331.
Bicarbonate of lime and sulphate of lead, 40.
Bineau on insolubility of protoxide of lead in water, 16.
Biot on melting-point of lead, 8.
Birmingham, quieking glass in, 1.
Bischof's process for extracting lead from carbonated ores, 434.
Bismuth and litharge, 20, 201, 202.
——, colours on melted lead affected by, 464.
Bitartrate of potash as a flux, 106.
Black litharge, 201.
Black oxide of manganese and sulphide of lead, 54.
Blackett, Mr., composition of his refined lead, 494.
Blast-furnace for air-reduction process, 220, 222; ore-hearth, 222, 278; for roasting and deoxidizing process, 298; for iron-reduction process, 357.
—— (Ore-hearth), 278.
—— "nose," 371.
—— (Rachette), 385.
—— (Slag-hearth), 412, 417.
——, reduction of litharge in, 476; of sulphate of lead, 433.
——, fume from, 454.
——, with charcoal or coke fuel, 482.
—— compared with reverberatory furnace, 491.
Bleiberg, lead-smelting at, 261.
——, wages at, 267.
——, assay of lead at, 270.

Bleiberg, American ore-hearth at, 292.
—— of Commern, 350.
—— furnace, 222, 261; modified, 270; at Friedrichshütte, 363; reduction of litharge in, 473.
—— lead, composition of, 267.
" Bleierde," 99.
" Bleiglanz," 94.
" Bleischwamm," 9.
" Bleispath," 99.
" Bleistein," 306.
" Bleivitriol," 98.
Blende with galena, 95.
—— from Przibram veins, 398.
—— and galena, silver in, 399; in Spence's process, 405.
—— in blast-furnace, 484.
" Blicksilber," 196, 209.
Blowing-machines in China, 480.
Blue-gum, 524, 526.
Blue-lead, 96.
" Bluestone " in the Isle of Man, 405.
Blue-vitriol made from copper-regulus, 333.
——, enriched regulus in manufacture of, 335.
Bodemann on Clausthal and Zellerfeld lead-ores, 369.
—— on lead-regulus, 373; on regulus from smelting of lead-regulus, 383.
—— on lead-speise, 376.
Bog Mine lead for red-lead making, 516.
Bohemia, lead-smelting in, 398.
Boles in Derbyshire, 215, 216.
" Boliche," 222, 247.
Bolivia, smelting at high elevations in, 277.
Bolley on action of pressure on finely-divided lead, 9.
Bone-earth, fluor-spar a flux for, 185.
Bonsdorff on solubility of protoxide of lead in water, 15, 16.
Bontemps' glass, 35.
Borax and sulphate of lead, 43.
—— in assay of galena, 106.
Borosilicate of lead, platinum vessels for, 28.
Bostrichus capucinus, lead perforated by, 521.
Böttger on peroxide of lead, 26.
Boudehen, M., his machinery for Pattinson's process, 143.
Boulanger on Bleiberg lead-smelting, 268.
Boulangerite, 98.
Boullay on specific gravity of red-lead, 24.
Bournonite, 98.
Bouteille, M., his exhibition of cartridges gnawed by insects, 522.
Bowen, Mr., his drawings of cupelling-furnaces, 178.
Braid, Mr., on lead-miners and lead-poisoning, 524.
" Brandsilber," 209.
Braubach, dezincification of lead at, 172, 174.
——, composition of lead from, 495.
Brendecke on insolubility in water of protoxide of lead, 16.

Bretagne, lead-smelting at, 244.
Breymann on copper-slag for reduction of galena, 387.
Bricks of " laja " in Spanish furnace, 247.
Brigantian lead, 214.
Britain, galena in, 95.
——, lead-smelting in, 213.
British lead-ores, 100; silver in, 102.
—— lead-smelters, 497.
British Museum, ancient pigs of lead in, 213.
Brittany, lead-smelting in, 244; furnace, 244.
Bromeis on lead-regulus from Lautenthal, 373.
Brooke and Miller on Jamesonite, 98.
Brooks on slag from smelting of regulus, Freiberg, 317.
" Brouse," 415, 416.
Brown iron ore with galena, 95.
Brüel on Clausthal and Zellerfeld lead-ores, 369.
—— on lead-regulus, 373; on regulus from lead-regulus, 383.
Brunner on " Naples Yellow," 87, 88.
Brush, Prof., on lead-smelting in United States, 278.
——, on cessation of lead-mining at Rossie (New York), 290.
——, on cost of lead from high and low furnaces, Friedrichshütte, 365.
Brushwood as fuel for " boliche," 252.
Buccleuch, Duke of, lead-fume condensing at his works, 444.
Buckley fire-bricks for furnaces, 228.
Bullets, rods of lead for making, 3.
—— American hunters' preparation of lead for, 213.
—— eroded by insects, 521.
" Bullet-spray," cows poisoned by, 532.
Burat on French mining enterprise, 338.
Burgfey, lead-smelting at, 357.
" Burnt " litharge, 13.
Buttons made of quicked glass, 2.

C.

Cadmium, action of, on nitrate of lead, 11.
Caermarthenshire, lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
Cahen, M., on Belgian compared with Flintshire furnace, 245.
Calamine with galena, 95.
Calcination, effect of zinc-blende in, 484.
—— at Freiberg, 307.
Calcite with galena, 95.
Calcium, fluoride of. *See* Fluoride of calcium.
Callidium sanguineum, lead perforated by, 522.
Calvert on crystallized protoxide of lead, 14.
—— and Johnson on dilatation of lead by heat, 8.

CAMPANULA.

Campanula rotundifolia in lead-bearing soil, 215.
Carbide of lead, 67.
Carbon and sulphate of lead, 51; with carbonate of lime and fluoride of calcium, 44.
—— and sulphide of lead, with fixed alkalies or their carbonates, 54; with baryta, 55; with lime, 55; with oxide of iron, 58; with lead, 67.
—— in slag- and ore-smelting, 325.
——, calorific power of, 349.
Carbonate of ammonia and sulphate of lead, 40.
—— of iron with galena, 95; in lead-ore, 488.
—— of lead, 99.
—— ——, its colour when heated, 13.
—— ——, assay of, 112.
—— ——, ores containing, 433.
—— ——, herbage and water affected by, 530.
—— of lime, with charcoal and silicate of protoxide of lead, 33; with fluoride of calcium, carbon, and sulphate of lead, 44.
—— ——, its influence in assay of galena, 113.
—— ——, in lead-ore, its effect on smelting, 487.
See Bicarbonate.
——, neutral, of protoxide of lead, 70.
—— of potash and sulphide of lead, 53.
—— of soda, with charcoal and silicate of protoxide of lead, 33; with sulphide of lead, 53.
—— —— in assay of lead-ore, 106.
Carbonates, fixed alkaline, and sulphate of lead, 40, 42.
—— of protoxide of lead, 67.
Carbonic acid from sulphate of baryta and coke-dust, 334.
—— oxide and sulphate of lead, 52; and sulphide of lead, 52.
Cardiganshire ticketings, 496.
——, production of lead-ore, lead, and silver in, 498.
Carinthia, lead-smelting in, 254, 269.
——, composition of lead from, 494.
Carnarvonshire, production of lead-ore, lead, and silver in, 498.
Carniola, lead-smelting furnace at, 263.
Carnot, M., on coal for cupellation-furnace, 197.
—— on lead-smelting at Freiberg, 303, 308.
—— on loss in lead-slag smelting, 331.
—— on smelting-costs, 332.
—— on treatment of copper-regulus, 333–337.
—— on specific gravity of "brown oil," 335.
Carthagena, ancient mining in, 421.
—— furnaces, 418, 421.
Cartridges eroded by insects, 521.
Cassel-yellow, 81.
Cast-iron, its action as fuel, 349.
—— from copper-slag, 388; from lead-slag, 391.

CLAUSTHAL.

Cast-iron, use of, in Schlieg-smelting, 397.
—— bottomed furnace for softening hard lead, 459.
Cast sheet-lead, 500.
Casting tea-lead (Chinese method), 501.
—— plates of zinc (Waddell's method), 501.
—— lead for rolling, 503.
Catalonia, Carthagena furnace in, 429.
Caustic potash and sulphide of lead, 53.
—— soda and sulphide of lead, 53.
"Cawk" with galena, 95.
Ceruse, 68, 509.
Cerussite, 70, 99.
Chalcedony with galena, 95.
Chambers for condensation of lead-fume, 442.
Charcoal, with silicates of protoxide of lead, 31–34.
——, reduction of phosphate of lead by, 76.
Charge for assay of galena in iron crucibles, 106.
—— for assay of carbonate and phosphate of lead, 112.
Charles II., his order for sheathing ships with milled-lead, 502.
Chemical properties of lead, 10.
Cheshire, lead-smelters in, 497.
Childrey, J., on lead-smelting in Derbyshire, 215.
Chimneys for condensing lead-fume, 434.
China, reduction of litharge in, 479.
China-clay and litharge, 489.
Chinese tea-lead, 463, 464; preparation of, by casting, 501; used for pipes, 507.
Chloride of ammonium and sulphide of lead, 66.
Chloride of lead, 77, 100; with sulphate of lead, 43; with arseniate of protoxide of lead, 74; with phosphate of protoxide of lead, 77.
—— ——, &c., dezincification of lead by, 160.
—— of potassium and sulphate of lead, 43.
—— of sodium with sulphate of lead, 43; with sulphide of lead, 65.
—— ——, dezincification of lead by, 161.
Chlorine and lead, 77.
Chlorocarbonate of lead, 84.
Christison, Dr., on lead-poisoning, 523; among miners, 524; among compositors, 525.
Cinnabar, 508, 528.
Claremont, lead-poisoned water at, 527.
Classification of smelting processes, 219.
Clausthal, desilverization of lead by zinc at, 159.
——, dezincification of lead at, 161.
——, desilverization by zinc at, 165.
——, dezincification by sulphuric acid at, 165.
——, Flintshire furnace at, 244.
—— lead-ores, 369.
——, lead-smelting with iron at, 370.
——, lead-regulus from, 373.
——, crystallized sulphide of lead from, 377.

CLAUSTHAL.

Clausthal, crystallized alloy from furnace at, 378.
——, regulus-smelting at, 383.
——, slags from Schlieg-smelting at, 394.
——, reduction of litharge at, 477.
—— clay, 478.
—— hard lead, 478.
——, analyses of lead at, 493.
——, composition of lead from, 493.
Clay used at Clausthal, composition of, 478.
—— in lead-ore, its effect on smelting, 489.
Clichy, white-lead made at, 69.
Cloud, Mr., on solubility of protoxide of lead in water, 16.
—— on sulphide of lead with sulphide of antimony, 38; with tribasic silicate of protoxide of iron, 58; with copper, 61; antimony, 62; with chloride of ammonium, 66.
—— on hyposulphite of soda and sulphate of lead, 42.
—— on sulphide of antimony and lead, 62.
—— on lead and arsenic, 71; and phosphorus, 74, 75; potassium, 89; sodium, 90.
—— on phosphates of lead, 76.
Clowes, Messrs., on compositors and type-poison, 523.
Coal, German cupellation with, 204.
——, first use of, for smelting, 218.
—— used in "boliche," 247, 252; in English furnace in Spain, 252.
Coal-fields in Spain, 428.
"Coarse" litharge, 13.
Cobalt with galena, 95; in iron, 96.
—— and nickel in speise, 318.
Cohesion of lead compared with welding of iron, 9.
Coke-dust in slag- and ore-smelting, 325.
—— and sulphate of baryta, carbonic acid from, 334; white-lead from, 334.
"Coke-stones" in Clausthal litharge-reduction furnace, 477.
Collet-Descostils on sulphide of lead, 37; and hydrogen, 52.
Colour of lead, 1.
—— of litharge, 12.
—— of carbonate of lead when heated, 13.
—— of red-lead when heated, 13; of orange-lead, 13.
—— of silicates of lead, 28, 29.
Colouring oven for red-lead making, 511; colouring tools, 513.
Colours on surface of melted lead, 463.
Columnar fracture of lead, 2.
Commern, desilverization of lead by zinc at, 158.
—— lead-ores, smelting, 350.
——, composition of lead from, 495.
Composition of bismuthic litharge, 202.
—— of charge for Flintshire furnace, 235; of grey-slag, 235.
—— of slag from ore-hearth at Keld Head, 282.

COST.

Composition of charge for smelting at Sala, 298, 300; at Tarnowitz, 362.
—— of regulus from lead-slags and ores with carbon, 325.
—— gas-pipes, 507.
See Analyses.
Compositors, effect of type-metal on, 525.
Condensation of lead-fume, 434.
Conductivity of lead for heat and electricity, 8.
Conflans, lead-fume from, 454.
Cookson, Mr., his use of iron in lead-smelting, 359.
Copper, dioxide of, with protoxide of lead, 17.
——, oxide of, sulphide of lead with, 534.
——, protoxide of, with protoxide of lead, 17.
—— and litharge, 21; and sulphide of lead, 60; lead, 91, 92; tungsten, 93.
—— in galena, 95; in litharge, 201.
——, its influence upon assay with fluxes in iron crucible, 117.
—— in Pattinson's process, 138, 146, 147.
——, its separation from lead by crystallization, 144.
——, elimination of, in cupellation, 202.
——, antimony and nickel alloy from smelting-furnace, 378.
—— and lead-slags, assays of, 389.
—— in Snailbeach lead, 508, 516.
—— in lead, its effect in making red-lead, 518.
——, concentration of, in unoxidized lead, 519.
Copper-ore slags, Schlieg-smelting with, 392.
Copper-pyrites with galena, 95; in lead-ore, its effect on smelting, 483.
Copper-regulus, treatment of, at Freiberg, 317, 333.
Copper-slag for reduction of galena, 385, 387; reducibility of iron in, 388.
——, cast-iron from, 388; pig-iron from, 390.
Corduriè's process, 167; at Havre, 169; at Lautenthal, 172, 535; at Mechernich, 171.
Coriolis on resistance of lead to pressure, 4.
Cornish crucible for assaying lead-ore, 104.
—— process of smelting in flowing-furnace, 257.
Cornwall, lead-smelting in, 218.
—— ticketings, 496.
——, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Cost of a boliche, 254; Carthagena furnace, 423; Fallize's lead-fume condenser, 446; Spanish slag-hearth, 417.
—— of desilverization at Tarnowitz, 157; desilverization by zinc at Clausthal, 165.
—— of litharge production in cupellation, 209.
—— of Pattinson's process, 139; of Parkes' process, 153.

Cost of reduction of grey-slags, 429; of dross, 467, 475; of litharge, 473, 478.
—— of smelting in ore-hearth, 291; in reverberatory furnace compared with ore-hearth, 284; in high and low furnaces, 365; in Carthagena furnace, 418, 427, 429; in Flintshire furnace in Flintshire, 496.
—— of smelting operations at Alguira, 255; Almeria, 255; Andalusia, 255; Flintshire, 496; Freiberg, 332; Pontgibaud, 345; Rossie, 291; Poullaouen, 245; Tarnowitz, 365, 475, 478.
—— for workmen at Bleiberg, 267; in Peru, 273; for Rachette furnace, 395.
Cotunnite, 77.
Courage, Mr., his use of steam for lead-fume condensing, 446.
Cows, lead-poisoning of, 530, 531.
Crane at Llanelly Lead-works, 127.
"Crasses blanches," 423.
Cream of tartar as a flux, 106.
Crimea, erosion of cartridges in the, 521.
Cromford, Matlockite found at, 79.
Crucibles for assaying lead-ore, 104.
——, Cornish, for preparing silicates of lead, 28, 31; subsulphide of lead, 39; sulphate of lead, 41.
——, Earthen, effect of protoxide of lead on, 15.
—— ——, assay of lead-ores in, with iron, 110.
—— ——, for assay of carbonate and phosphate of lead, 112.
——, Hessian, for preparing "Giallolino," 87.
—— —— for assaying lead-ore, 104.
——, Iron, used at the Royal School of Mines, 104, 108.
—— ——, assay of galena in, with fluxes, 106.
—— ——, assay of lead-ores in, without fluxes, 110.
—— ——, influence of metals upon assay with fluxes in, 117.
——, Platinum, fusion of protoxide of lead in, 15.
—— ——, for silicates of protoxide of lead, 28.
——, Silver, fusion of protoxide of lead in, 15.
Crust from oxidation of lead and copper, 92; on lead-pipe, 535.
Crystalline system of lead, 1.
—— oxide of lead, reduction of, 15.
Crystallization, desilverization of lead by, 121.
——, elimination of metals from lead by, 144.
—— of sulphate of copper from regulus, 336.
Crystallized protoxide of lead, 13; chloride of lead, 77.
Crystals of lead in quicking glass, 1.
—— of litharge, 12.

Crystals of sulphide of lead, 37.
—— of lead, from Pattinson's process, 67.
—— of lead-regulus in Upper Harz, 372.
—— (furnace) of sulphide of lead, 377.
Cumberland, lead-smelting in, 216.
——, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Cupellation, 121, 177.
—— (English), 178; loss of lead in, 185.
—— (German), 185; with coal as fuel, 204; accessory products from, 370; melting black litharge in, 478.
——, lead-fume collected during, 455, 457.
Cupola, Derbyshire, 216.
Cupriferous lead, liquation of, 91.
Curaudeau on oxychloride of lead, 80.
Cyanide of potassium and sulphate of lead, 45; and sulphide of lead, 63.

D.

Dalton on melting-point of lead, 8.
Davy, Sir H., on red-lead of the ancients, 508–9.
Day, Dr., his accident at a lead-condensing flue, 437.
Decopperization of lead by zinc, 174, 519.
—— of Derbyshire slag-lead, 176.
Dee Bank, Stagg's condenser at, 441.
Delgado, J. M., inventor of Carthagena furnace, 421.
Denbighshire ticketings, 496.
——, lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
Deoxidation of oxidized ores of lead, 220.
Deoxidizing and roasting process, 296.
Derbyshire, lead-smelting in, 214–217, 278.
——, ore-hearth in, 278.
——, smelting old lead-slags in, 418.
—— "linnets," 433, 434.
——, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
——, lead-poisoning of animals in, 530.
Desilverization of lead — by crystallization, 121; by zinc, 148; by cupellation, 177.
—— at Clausthal, 165; at Mechernich, 354.
Desmarest, M., on erosion of lead by insects, 521.
Desulphurization of galena, 219.
Deville, C. Sainte-Claire, on specific gravity of lead, 4.
Devonshire, production of lead-ore, lead, and silver in, 498.
Dezincification of lead by chloride of lead, &c., 160; by litharge, 172.
—— of desilverized lead by steam, 167.
See Zinc.
Dicarbonate of lead, 68.
Dick, Mr., pure lead prepared by, 3.
—— on subsulphide of lead, 39.

DICK.

Dick, Mr., on sulphide of lead and vapour of water, 54; and tin, 59; copper, 60.
—— on yellow antimoniate of lead, 87.
—— on crystals in Pattinson's process, 131; on limit of concentration in the process, 138.
—— on amount of lead refined on certain test, 184.
—— on black litharge, 201.
—— on action of charge on furnace-bed, 236.
—— on action of lime in Flintshire furnace, 238.
—— on "Boliche," with coal-fuel, 247.
—— on "Horno reverbero," 247, 254.
—— on smelting at La Fortuna, 252.
—— on alloy from liquation of hard lead, 468.
Dilatation of lead by heat, 8.
Dioxide of lead, 11.
—— of copper with protoxide of lead, 17.
Dishes, iron, assay of galena in, 108.
Disulphide of copper (argentiferous), sulphate of copper from, 337.
Dixon, Capt., on lead-smelting in India, 293.
Dobbs' patent for adhesion of tin and lead, 9.
Dollond, Mr., his table of the composition of optical glass, 35.
Dolomite with galena, 95; in lead-ore, its effect on smelting, 488.
——, hearth-bed of, 206.
Double furnaces at Bleiberg, 263.
Double sulphides of lead and sodium or potassium, 38.
Dressing lead-ores, at Commern, 351; at Sala, 297.
Dross, reduction at Tarnowitz, 473.
—— from softening of hard lead, 466.
Drossing by machinery, 517; action of slag-lead in process, 517.
Drossing-oven for red-lead making, 509; concretionary matter from, 520.
Drossing-tools, 513.
Du Boys, M., his type-metal perforated by insects, 521.
Ductility of lead, 2.
Dumfries, lead-smelters in, 498.
Durham, lead-smelting in, 216.
——, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Dutch white-lead manufacture, 68, 70.

E.

Earthen crucibles, effect of protoxide of lead on, 15.
—— ——, assay of lead-ores, in, with iron, 110.
—— —— for assay of carbonate and phosphate of lead, 112.
Ebner and Co., their furnace at Bleiberg, 262, 266.

FLACH.

Egypt, use of "alquifoux" in, 94.
Eich on slagged ore at Münsterbusch, 356.
Eifel, desilverization of lead by zinc in the, 158.
—— works, residues from argentiferous lead at, 163.
See Commern.
Elasticity of lead, 2.
Electricity, conductivity of lead for, 8.
——, protoxide of lead a conductor of, 15.
Ems, lead-smelting at, 356.
——, crystallized alloy from, 378.
Enamel colour, Naples yellow used for, 88.
England (north of), ore-hearth in, 278; slag-hearth in, 411; Spanish slag-hearth in, 418.
——, indebted to foreign workmen, 364.
——, list of lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
——, lead-smelting in, in the 17th century, 537.
English cupellation, 178.
—— furnace with coal, in Spain, 252.
—— lead, analyses of, at Clausthal, 497.
Erosion of lead by insects, 521.
Eschka, M., analysis of Abstrich by, 201.
—— on Przibram lead-ores, 399.
Eschweiler Co., composition of their lead, 495.
"Esparto," 425.
Estremadura, Carthagena furnace in, 429.
Export of lead from the United Kingdom, 499.
Extraction of silver from lead, 121; from zinc, 163.
Ey, his drawings of Rachette furnace, 385.
—— on lead from Rachette furnace and Schliegofen, 393; on regulus, 393.

F.

Fadé and Co., composition of their lead, 495.
Fahlore with galena, 95.
Fahlun, pyrites in magnetic ore at, 326.
Fallize, M., his plan for condensing lead-fume, 444.
—— on lead from fume, 457.
Falmouth, smelting in flowing-furnace at, 257, 260.
Faraday, his use of platinum vessels for borosilicate of lead, 28.
—— on composition of optical glass, 35.
Farey on ancient boles, 215.
—— on cupola furnaces, 217.
"Feinbrennen," 209.
Ferientsik on Bleiberg lead, 267.
Ferrocyanide of potassium and sulphide of lead, 63.
Figari Bey, Dr., on "archifoglio," 94.
Fire-bricks, Buckley, for furnaces, 228.
Fixed alkalies. *See* Alkalies.
Flach, his process for extracting silver from lead, 162; Sieger on the process, 164.

"Flake" litharge, 13.
—— white, 68.
Flint-glass, substitute for minium in making, 43.
——, the best red-lead for making, 507, 516.
Flintshire, lead-smelting in, 216–240.
—— ticketings, 496.
——, lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
Flintshire-furnace, smelting in the, 218, 222.
——, with Stagg's condenser, 441.
—— at Adra, 244; Alport, 240; Bagillt, 229; Belgium, 245; Clausthal, 244; Peru, 274; Tarnowitz, 242, 366.
—— in Flintshire, cost of smelting in, 496.
Flowing-furnace, 218, 222.
—— in Cornwall, 257; in Wales, 261.
——, Australian lead-ore in, 430.
Flues for lead-fume condensation, 437.
Fluor-apatite with pyromorphite, 100.
Fluor-spar with galena, 95.
—— in assay of lead-ore, 106.
—— a flux for bone-earth, 185.
——, its use for flux at Alport, 240.
—— not used now at Par and Point, 260.
—— in lead-ore, its effect on smelting, 488.
Fluoride of calcium with sulphate of lead, 44; with sulphate of lead and lime, 44; with sulphate of lead, carbonate of lime, and carbon, 44; with sulphates of lead, baryta, and lime, 44.
Fluxes for assay of lead-ore, 106.
——, assay of galena in iron crucibles with, 106.
——, assay of lead-ores in iron crucibles without, 110.
—— in iron crucible, influence of metals upon assay with, 117.
—— for bone-earth, 185.
——, fluor-spar used as, at Alport, 240.
Forbes, Mr. D., on smelting at high elevation, 277.
Ford on argentiferous galena at Carthagena, 422.
Foreign countries, production of lead in, 499.
—— lead, analyses of, 493–495.
Forster on boles, 216.
Foster on lead-condensing flues, 438.
"Fourneau à manche," 412.
Fournet on cohesion of lead, 9.
—— on volatilization of protoxide of lead, 15.
—— on arseniuretted lead, 71.
—— on subsulphides of lead, 40.
—— on sulphide of lead and iron, 57; and tin, 60; zinc, 61; antimony, 62.
—— on sulphide of arsenic and lead, 63.
France, production of lead in, 338, 499.
——, Carthagena furnace in, 429.
Franke on bismuthic litharge, 202.
Franks, Mr., on Roman lead, 213.
Franz on conductivity of lead for heat and electricity, 8.

Freiberg, octahedral crystals in lead from, 2.
——, cost of Pattinson process at, 139.
——, German cupellation at, 186.
——, lead-smelting at, 303; in the blast-furnace, 309; in reverberatory furnace, 319; yields and loss, 330; costs, 332.
——, fraudulent use of lead-smelters' names at, 303.
——, treatment of copper-regulus at, 333.
—— mines, produce of, 337.
——, softening hard lead at, 460.
——, reduction of litharge at, 476.
Fremy on crystallized protoxide of lead, 13.
—— on peroxide of lead, 25.
French crucible for assaying lead-ore, 104.
Fresenius on sulphate of protoxide of lead, 40.
—— on German and Spanish lead, 495.
Freycinet, M. Roux de, inventor of Spanish slag-hearth, 418.
Friedrichshütte. *See* Tarnowitz.
Fuel for assay of lead-ore, 104.
—— for German cupellation process, 197; use of coal as, 204.
——, first use of pit-coal for, in smelting, 218.
——, plants used for, in Spanish smelting-works, 256.
—— for Bleiberg furnace, 262, 263, 266; for boliche, 252; Carthagena furnace, 424; Flintshire furnace, 230, 242; ore-hearth, 291; slag-hearth, 414.
—— used by Keld Head Mining Co., 281.
—— for smelting at Freiberg, 309; Pontgibaud, 345; Sala, 298; Tarnowitz, 364.
——, saving of, by roasting lead-regulus in kilns, 393.
—— for smelting-furnaces, general remarks, 482.
Fume of lead. *See* Lead-fume.
Furnace accretions, 376.
——, Air, 213–215, 421.
——, Assaying, 104.
——, Blast. *See* Blast-furnace.
——, Bleiberg, 222, 261.
——, brick, for softening hard lead, 462.
——, Carthagena, 421.
——, Cupellation, at Llanelly, 178; at Freiberg, 185; at Friedrichshütte, 204; Przibram, 479.
——, Double, 263.
——, Flintshire, 218–245. *See* Flintshire-furnace.
——, Flowing, 218, 222; in Cornwall, 257; in Wales, 261.
——, German cupellation, 185, 204, 479.
——, Half-high, 400.
——, High, 362.
——, Kramer, 400.
——, Liquation, 469.
——, Low, 360.
——, Rachette, 385.
——, Reverberatory, 216. *See* Reverberatory-furnace.
——, Seven-twyer, 314–316.

Furnace, Softening, 459.
——, Spanish, 222, 246.
——, Stolberg, 314.
——, Treble, 268.
Furnace-bottom, of cast-iron, for softening-furnace, 459.
——, of dolomite, and of lime-marl, for German cupellation-furnace, 185, 188, 190, 205.
——, of grey-slag, for Flintshire furnace, 228.
——, of "laja" bricks, for Spanish furnace, 247.
Furnace-bottoms, crystallized compounds in, 325.
Furnace-charges. *See* Charges.
Furnace-lead, Upper Harz, 372.
Furnaces, lead-fume from, 436.
—— for lead-smelting, choice of, 490.
See under Lead-smelting.
Fusibility of lead, 8.
—— of silver, 15.
—— of protoxide of lead with metallic oxides, 17.

G.

Galena, 37.
——, specific gravity of, 37.
——, action of water on, 37.
——, substitute for, in pottery glazing, 43.
—— and vapour of water, 51.
——, use of iron for assay of, 56.
——, description of the ore, 94.
——, British localities of, 95.
——, metals associated with, 95; silver in, 95–97.
—— in anthracite, 95; in sandstone, 352.
——, association of gold and silver with, 96.
——, effect of washing on, 96.
——, assay of, in iron dishes, 108; in iron crucibles, with fluxes, 106; influence of non-metalliferous matters upon yield of, 113.
——, influence, in assay of, of carbonate of lime, 113; of silica, 114; of sulphate of baryta, 116.
——, desulphurization of, 219.
——, smelting by air-reduction process, 220.
—— in Flintshire furnace, 239, 244.
——, increased amount raised at Linares, 247.
——, effect of free silica in smelting, 346.
——, reduction of, by iron, 357.
—— added to bath of lead in German cupellation-furnace, 364.
—— from Friedrichsgrube used at Tarnowitz, 366.
—— of the Upper Harz, 369.
——, copper-slag for reduction of, 385.
—— and blende, silver in, 399; in Spence's process, 405.
——, argentiferous, of Carthagena, 422; of Peru, 271, 273; of Przibram, 398; of Sala, 303.

Galena, reduction of, in ore-hearth, 481.
——, iron-scales heated with, 483.
Gas-pipes, tea-lead used in making, 507.
Gay-Lussac, M., on sulphate of lead and carbon, 51.
—— and Thénard, MM., their alloy of lead and potassium, 88.
—— —— on lead and sodium, 90.
Geocronite, 98.
German cupellation, 185; with coal as fuel, 204; accessory products from, 370; melting black litharge in, 479.
—— lead, composition of, 495.
—— litharge, 203.
—— proverb on lithargification, 190.
German States, production of lead in, 499.
"Giallolino," 87.
Gibb, Mr., on smelting in Cornish flowing-furnace, 261.
Gladenbach, galena with manganese from, 95.
Glamorganshire, lead-smelters in, 498.
Glanvil on lead-smelting in England in the 17th century, 537.
Glass, quicking, 1.
——, optical, 35.
——, flint, substitute for minium in making, 43.
——, the best red-lead for making, 507, 516.
"Glasurerz," 94.
Gmelin on dicarbonate of lead, 68.
—— on Cassel-yellow, 81.
Göbel on chloride of lead, 79.
Gold in galena, 95–97; in lead-fume, 455; in litharge, 201.
——, its influence upon assay with fluxes in iron crucible, 117.
Gossage, Mr., white-lead made by, 69.
Gout induced by lead-poisoning, 526.
Grailich on crystals of litharge, 12.
Grandison, Lord, his process for smelting in reverberatory furnace, 218.
Grass near lead-works, carbonate of lead in, 530.
Greece, production of lead in, 499.
"Green linnet," 99.
Green's optical glass, 35.
Greenwich Hospital Estate, pig-lead from, 508.
Grey-slags. *See* Slags.
Grimm on silver in Przibram blende, 399.
—— on lead-smelting at Przibram, 402–404.
Grote, Mr., on the Attic drachma, 422.
"Grün-Braunbleierz," 99.
Gruner, M., on zinc and chloride of lead, 160.
—— on Brittany process, 244; on Cordurie's process, 169, 171.
—— on dezincification of lead at Braubach, 174.
—— on the ore-hearth, 480.
—— on iron-reduction process, 485.
——, his general conclusions on lead-smelting, 491.

Guenneau de Mussy, Dr., his sulphur-baths for lead-poisoning, 527.
Guignand's glass, 35; composition similar to, 36.
Guy's Hospital, treatment of lead-colic at, 526; of lead-palsy, 527.

H.

Hag-hill or Hag-bank, fuel for boles taken from, 216.
Hahn, Dr., on lead-regulus, 373.
—— on lead from revived litharge, 493.
"Halbhochofen," 400.
"Half-high" furnace at Przibram, 400.
Hall, W., on softening hard lead, 462.
Hannibal, silver from Carthagena obtained by, 422.
Hard lead softening, 458; brick furnaces for, 462; dross from, 466.
——, liquation of, 467.
——, English, 466; Spanish, 467.
——, production of, at Przibram, 479; in the Upper Harz, 478.
See Slag-lead.
Hardness of lead, 2.
Harz, litharge crystals from, 12.
——, Cordurie's process in, 535; Parkes' process, 171.
——, lead-smelting in seven-twyer furnace in, 316.
——, lead-smelting with copper-slags in, 385; with iron, 368.
——, reduction of litharge in, 478.
—— lead, analyses of, 494.
Hausmann on crystals of litharge, 12.
—— on sesquioxide of lead, 23.
—— on tarnish of furnace-crystals, 377.
—— on crystallized alloy from smelting-furnace, 378.
—— on sulphate of lead in lead-smelting, 381.
—— on lead-regulus from Upper Harz, 374.
Havre, Cordurie's process at, 169.
Hearth-bed, dolomite, at Tarnowitz, 205.
Hearth-ends, treatment of, 289.
Hearths, Slag. *See* Slag-hearths.
Heat, conductivity of lead for, 8.
——, dilatation of lead by, 8.
——, latent, of lead, 8; specific, of lead, 8.
—— for reduction of protoxide of lead, 15.
Hedyphane, 100.
Henkel, Dr., on cast-iron from copper-slags at Altenau, 388.
Henry, Mr., his drawings of Pattinson's apparatus, 124.
—— on Australian lead-ore, 430.
——, his specimens of lead-fume, 451.
Herbst and Co., Parkes' process at works of, 158; composition of their lead, 495.
—— and Wassermann, their patent for dezincification of lead by chloride of lead, 160.
Herder, Von, on lodes at Freiberg, 304.

Heron, Mr., on manufacture of red-lead, 512, 514.
Hessian crucible used for preparing "Giallolino," 87.
—— —— for assaying lead-ore, 104.
Hilgenberg, Dr., on cast-iron from lead-slag, 391.
—— on slags from Schlieg-smelting in Rachette furnace, 394.
Himmelfahrt mine, 304.
History of lead, 1; of red-lead, 508.
Hochstätter, Mr., on lead and manganese, 94.
—— on Cordurie's process, 171.
—— on lead-smelting at Commern, 350; at Freiberg, 320, 322, 331, 333; at Mechernich, 171, 352.
—— on smelting lead-slags, 320, 322; on loss in smelting, 331.
—— on smelting copper-regulus, 333.
Hodges, J., his process for smelting in reverberatory furnace, 218.
Holmes's optical glass, 35.
Holywell, Stagg's condenser at works near, 441.
—— Lead-works, red-lead making at, 515.
——, immunity of miners at, from lead-poisoning, 524.
Holzappel, machinery applied to Pattinson's process at, 143.
——, lead-smelting at, 244.
——, crystallized alloy from, 378.
Hong Kong, litharge-reduction at, 479.
Hornblower, Mr., on Spanish slag-hearth, 419.
Horn-lead, 78.
"Horno reverbero," 247.
"Hornos de Gran Tiro," 421.
Horses, lead-poisoning of, 530, 531.
Hughes, Mr., his apparatus for rolling lead, 504–506.
Hunt, Mr. Robt., on yield of silver from British lead-ores, 102.
Hydrated protoxide of lead, 22.
Hydrochloric acid as a solvent of lead, 10.
—— and sulphide of lead, 38; and sulphate of lead, 40.
—— applied to white-lead manufacture, 81.
—— for extraction of lead from carbonated ores, 434.
Hydrogen and sulphate of lead, 52; and sulphide of lead, 52.
Hyponitrates of protoxide of lead, 85.
Hyposulphite of soda, action of, on sulphate of lead, 42.

I.

Ihle, his octahedral crystals of lead, 2.
——, on copper-regulus, 317.
Illig on dezincification of lead, 160, 162.
—— on desilverization by zinc, 167; elimination of metals in process, 176.
Implements for assay of lead-ore, 104.
Import of lead into the United Kingdom, 499.

INDIA.

India, lead-smelting in, 213; in blast-furnace, 293.
Indian method of refining, 211.
Insects, perforation of lead by, 521.
Insolubility of protoxide of lead in water, 16.
International Exhibition (1851), Pattinson's ladle in, 127.
—— ——, model of lead-fume condenser in, 444.
—— —— (1862), lead of columnar fracture in, 3.
—— ——, white-lead from decopperized Derbyshire slag-lead at, 176.
Iodide of potassium, use of, for lead-palsy, 527.
Ireland, lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
——, Mining Company of, red-lead manufacture by, 514.
Iron, welding of, compared with cohesion of lead, 9.
—— and litharge, 21.
——, silicates of protoxide of lead with, 33.
—— and lead, double sulphides of, 38.
—— and sulphate of lead, 45.
—— and sulphide of lead, 56.
—— as a reducing agent in lead-smelting, 56.
—— in copper-slags, 388; in galena, 95.
——, nickel, and cobalt, 96.
—— in assay of lead-ore, 106; in assay in iron crucibles, 110; in assay with fluxes in iron crucible, 119.
——, elimination of, in cupellation, 202.
——, reduction of silicate of lead by, 533.
——, Basic silicate of protoxide of, lead-smelting with, 384; tribasic silicate and sulphide of lead, 58.
——, Carbonate of, with galena, 95; in lead-ore, its effect on smelting, 488.
——, Cast. *See* Cast-iron.
—— Crucible used at the Royal School of Mines, 104, 108.
—— ——, assay of galena in, with fluxes, 106.
—— ——, assay of lead-ores in, without fluxes, 110.
—— ——, influence of metals upon assay with fluxes in, 117.
——, Protosulphide of, silicate of lead with, 31.
——, Sesquioxide of, with protoxide of lead, 17; with sulphide of lead, 56.
——, Sulphide of, heated with litharge, 533.
Iron-dishes, assay of galena in, 108.
Iron-finery slag, 360, 368, 384.
Iron-reduction process, 219, 485, 492.
—— —— in the Harz, 368; in Japan, 384; at Przibram, 398; at Tarnowitz, 357.
Iron-pots for Pattinson's process (cast-iron), 123; (wrought-iron), 139.

KERL.

Iron-pyrites with galena, 95; in lead-ore, its effect on smelting, 482.
Iron-scales with protoxide of lead, 17; with galena, 483.
Iron-work of ships in contact with lead, corrosion of, 502.
Isle of Man, lead-lodes in, 102.
—— ticketings, 496.
——, production of lead-ore, lead, and silver in, 498.

J.

Jacquelain on sesquioxide of lead, 23.
—— on peroxide of lead, 25.
Jamesonite, 98.
Japan, lead-smelting in, 384.
Jars on litharge-reduction furnace, 471.
Jewellers' "sweep" in flowing-furnace, 261.
Joachimsthal, composition of lead from, 493.
John on carbide of lead, 67.
Johnson, Mr., on dilatation of lead by heat, 8
—— on dissolving oxide of lead from cupels, 464.
Jordan (of Clausthal) on sulphide of lead with steam, 50; with lime and carbon, 55; sesquioxide of iron, 56; oxide of iron and carbon, 58.
——, Mr. T. B., his machinery for Pattinson's process, 141.
Joy on lead-regulus from Clausthal, 373.

K.

Kaolin and litharge, 489.
Kapnik, Abstrich from, 201.
——, elimination of antimony, copper, and iron during cupellation at, 202.
Karmarsch on tenacity of lead, 8.
Karsten on specific gravity of red-lead, 24.
—— on lead and copper, 91.
——, his experiments on Parkes' process, 153–158.
—— on the Bleiberg process, 269, 270.
—— on lead-smelting at Tarnowitz, 361, 368.
Kasr ruins (Babylon), enamelled brick from, 88.
Kast, inventor of "coke-stones," 477.
Keates, Mr., on slag for furnace-bed, 229.
——, on manufacture of red-lead, 512.
——, on commercial details relating to lead, 496.
—— and Henry, Messrs., on lead-smelting in Wales, 229.
—— ——, on products of smelting galena in Flintshire furnace, 239.
Keld Head, smelting process at, 279.
——, slag-hearth at, 412.
——, lead-fume condensation at, 442.
——, amount of lead from fume at, 456.
Kerl on refining in test with blast under muffle, 212.

KERL.

Kerl on lead-smelting in the Harz, 368–383.
—— on copper- and lead-slags, 389; on slags from Schlieg-smelting in Rachette furnace, 394.
—— on reduction of iron from slags, 397.
—— on Clausthal litharge-reduction furnace, 477.
—— on zinc-blende in calcination, 484.
—— on smelting lead-ore containing carbonate of lime, 487; iron, 488; silica, 487.
Kersten on marl furnace-beds, 185, 188.
Kilbrickenite, 38, 98.
Kilns, roasting lead-regulus in, 393.
Klasek on lead-regulus from lead-smelting at Przibram, 407.
Knappusche, lead-smelting furnace at, 263.
Köller on American ore-hearth at Przibram, 293.
Königshütte, litharge crystals from, 12.
——, treatment of copper-slags at, 389; of lead-slags, 390.
Kopp on dilatation of lead by heat, 8.
Kramer furnace, 400.
Kremnitz, composition of lead from, 493.
"Krummofen," 412.
Kupffer on specific gravity of lead, 3.
—— on melting-point of lead, 8.

L.

Laak, galena with anthracite from, 95.
La Carolina, furnaces at, 255.
Ladle, Pattinson's, 127.
La Fortuna, lead-smelting at, 252.
Lagerhjelm on elasticity of lead, 2.
"Laja" bricks in Spanish furnace, 247.
Lamborn, Dr., on lead-smelting in Missouri, 213.
Lanarkite, 100.
Lanarkshire, lead-smelters in, 498.
Lancashire, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Landgrebe on lead and phosphorus, 75.
Långbanshytta, pyromorphite from, 77.
Lange, his method of mixing zinc and lead in desilverizing, 157.
—— on lead-smelting at Tarnowitz, 360–368.
La Pise, lead-smelting at, 346.
Latent heat of lead, 8.
Laurium silver mines, 418.
Lautenthal, Cordurie's process at, 172, 535.
——, lead-smelting with iron at, 369.
——, crystallized lead-regulus from, 372.
——, lead-regulus from, 373.
——, roasting lead-regulus at, 382, 383.
——, Rachette furnace at, 387; first Rachette furnace for smelting Schlieg at, 395.
——, slags from Schlieg-smelting at, 394.
——, iron-reduction process at, 402.

LEAD.

Lautenthal, composition of lead from, 478, 493, 494.
Laxey, lead-lodes at, 102.
LEAD, history of, 1.
——, physical properties of, 1.
——, coating glass with, 1.
——, bullets from rods of, 3.
——, finely divided, pressed into solid mass, 9.
——, chemical properties of, 10.
——, atomic weight of, 10.
——, action of acids on, 10; of water, 10.
—— and antimony, 86; arsenic, 71; carbon, 67; chlorine, 77; nitrogen, 85; oxygen, 10 (*see* Oxygen); phosphorus, 74; silicon, 27; sulphur, 37.
——, dioxide or suboxide of, 11.
——, protoxide of, 12. *See* Protoxide of lead.
—— and metallic oxides, 16.
——, hydrated protoxide of, 22.
——, sesquioxide of, 23.
——, silicate of. *See* Silicate of lead.
——, sulphide of. *See* Sulphide of lead.
——, peroxide of, 24.
——, oxychlorides of, 79.
——, chlorocarbonate of, 84.
——, atmospheric influence on, 67.
——, gold and silver in smoke from, 96.
——, Alloys of, 88; with potassium, 88; sodium, 90; copper, 91; manganese, 93.
——, extraction of silver from, 121; Pattinson's process, 121; Parkes' process, 148; Cupellation, 177.
——, elimination of metals from, by crystallization, 144.
——, dezincification of, by chloride of lead, 160; by other chlorides, 161.
——, decopperization of, by zinc, 174, 519.
——, refining of, 177.
——, production of, in France, 338; at Sala, 303; in the United Kingdom, 498.
—— from regulus-smelting, 383; from Schlieg-smelting, 393, 397.
——, extraction of, from grey-slags, 412; from carbonated ores by wet process, 434; from lead-fume, 456.
——, hard, softening of, 458.
——, softened, poling of, 461.
——, liquation and poling of, 469.
——, pattinsonized, litharge from, 476.
——, production of, in the United Kingdom, 498; in foreign countries, 499.
——, imported and exported, 499.
——, corrosion of iron-work in contact with, 502.
——, casting of, for rolling, 503.
—— for pipes, 506.
—— for sulphuric acid chambers, 507.
—— for red-lead for glass manufacture, 507, 516. *See* Red-lead.
—— for white-lead, 508. *See* White-lead.
—— containing sulphur for making red-lead, 518.
——, unoxidized, concentration of copper in, 519.

LEAD, absorption of, and diffusion through the body, 526.
——, analyses of. *See* Analyses.
——, commercial details respecting, 496.
Lead-colic, 524, 526.
LEAD-FUME, condensation of, 278, 367, 434.
—— collected at Friedrichshütte, 367.
——, Fallize's scheme for condensing, 444.
——, characters and composition of, 451.
——, agglomerated, 454.
——, gold and silver in, 455.
——, quantity of, from smelting lead-ores, 456.
——, analyses of, from Alston Moor and Conflans, 454; Bagillt, 451; Pontgibaud, 452, 454; Villefort, 455.
—— condensing apparatus, 437; at Alport, 438; near Alston, 447; at Keld Head, 442; at Pontgibaud, 452; at Wanlock Head, 444.
Lead-mines, infrequency of lead-poisoning in, 523.
"Lead-moss," 3.
LEAD-ORES:—Galena, 94; anglesite, 98; cerussite, 99; pyromorphite, 99; mimetesite, 100.
—— of Ajmír, 293; Australia, 430, 538; Bleiberg, 266; Britain, 100, 433; Commern, 350; Freiberg, 304; Harz, 369; Linares, 247; Pallières, 346, 348; Pontgibaud, 339; Przibram, 398; Sala, 296; Sierra de Gador, 422; Tarnowitz, 358.
——, assay of, 103; wet assay, 120. *See* Assay.
——, general description, 218; silver in, 219.
——, oxidized, deoxidation of, 220.
——, carbonated, extraction of lead from, by wet process, 434.
——, foreign matters in, as affecting smelting, 480.
——, purchase of, 496.
——, production of, in the United Kingdom, 498.
Lead-palsy, 527.
Lead-pipe, 506; crust on, 535.
Lead-poisoning, 523. *See* Poisoning.
Lead-region of the United States, 278.
Lead-regulus. *See* Regulus.
Lead-residues treated in flowing-furnace, 261.
Lead, sheet (cast), 500; rolled or milled, 501.
Lead-shot, alloy for making, 71.
Lead-slags. *See* Slags.
Lead-smelters, British, 497.
LEAD-SMELTING, use of iron in, 56.
——, history of, 213.
—— in England in the 17th century, 537.
—— Processes:—Air-reduction, 220; roasting and deoxidizing, 296; iron-reduction, 357; variety of processes, 480.
—— in Air-furnaces, 213–215, 421.
—— in Blast-furnaces, 222; ore-hearth, 278; American ore-hearth, 289. *See also* Blast-furnaces.
Lead-smelting in Reverberatory furnaces, 222; Flintshire furnace, 222; Spanish furnace, 246; Flowing-furnace, 257; Bleiberg furnace, 261. *See also* Reverberatory furnaces.
—— Furnaces, choice of, 490.
—— with basic silicate of protoxide of iron, 384.
—— with copper-slags in Rachette furnace, 385.
—— condensation of lead-fume in, 436.
——, influence of foreign matters in the ore on, 480.
—— Works:—
Adra, 244, 247, 254, 423, 429.
Ajmír, 293.
Albertville, 244.
Alguira, 255.
Almeria, 255.
Alport, 240, 419, 433, 434, 438.
Alston, 447.
Alston Moor, 454.
Altenau, 188, 369, 382, 383, 385, 388–90, 394, 493, 494.
America, 213, 289.
Andalusia, 255.
Andes, 275.
Andreasberg, 174, 369, 370, 373, 376, 378, 383.
Arrayañez, 247, 252.
Asbach, 519.
Bagillt, 229, 239, 420, 430, 451.
Belgium, 139, 229, 245, 499.
Berja, 247, 254.
Bleiberg, 222, 261, 267, 270, 292, 350, 363, 473.
Bohemia, 398.
Bolivia, 277.
Braubach, 172, 174.
Brittany, 244.
Burgfey, 357.
Caermarthenshire, 498.
Cardiganshire, 496, 498.
Carinthia, 254, 269, 494.
Carnarvonshire, 498.
Carniola, 263.
Carthagena, 418, 421.
Catalonia, 429.
Cheshire, 497.
China, 479.
Clausthal, 159, 161, 165, 244, 369, 370, 373, 377, 378, 383, 394, 477, 478, 489, 493.
Commern, 158, 350, 495.
Cornwall, 218, 257, 496–498.
Cumberland, 216, 497, 498.
Dee Bank, 441.
Denbighshire, 496, 498.
Derbyshire, 214, 278, 418, 433, 434, 497, 498, 530.
Devonshire, 498.
Durham, 216, 497, 498.
Eifel, the, 158, 163. *See* Commern.

Lead Works:—
Ems, 356, 378.
England, 95, 100, 102, 213, 278, 364, 411, 418, 497, 498, 537.
Estremadura, 429.
Falmouth, 257, 260.
Flintshire, 216–240, 496, 498.
France, 338, 429, 499.
Freiberg, 139, 186, 303, 460, 476.
Friedrichshütte. *See* Tarnowitz.
German States, 499.
Glamorganshire, 498.
Greece, 499.
Harz, 171, 316, 385, 368, 478, 494, 536.
Havre, 169.
Holywell, 441, 515, 524.
Holzappel, 143, 244, 378.
Hong Kong, 479.
India, 211, 213, 293.
Ireland, 498, 514.
Isle of Man, 102, 496, 498.
Japan, 384.
Kapnik, 201, 202.
Keld Head, 279, 412, 442, 456.
Knappusche, 263.
Königshütte, 389, 390.
La Carolina, 255.
La Fortuna, 252.
Lanarkshire, 498.
Lancashire, 497, 498.
La Pise, 346.
Laurium, 418.
Lautenthal, 272, 369, 372–3, 382–3, 387, 394–5, 402, 478, 493–4, 535.
Laxey, 102.
Lead-hills, 24, 524.
Linares, 247, 252.
Llanelly, 127, 178.
Marseilles, 244.
Matlock, 241.
Maubach, 434.
Mechernich, 171, 352, 495.
Mendip hills, 497.
Merionethshire, 498.
Missouri, 213.
Montgomeryshire, 498.
Mühlengasse works, 354.
Münsterbusch, 355.
Nantes, 244.
Nent Head, 441.
Newcastle-on-Tyne, 81, 471.
New York, 289.
Northumberland, 216, 497–8.
Oker, 388, 393.
Par, 257.
Pembrokeshire, 498.
Peru, 215, 271, 273-4.
Point, 257.
Pontgibaud, 203, 338, 452, 454.
Poullaouen, 244, 487.
Prussia, 171.
Przibram, 293, 398, 479, 481, 493.
Ripon, 214.
Rossie (New York), 289.
Rothehütte, 389–90.

Lead-Works:—
Rouen, 143.
Sala, 296, 298.
Sardinia, 499.
Savoy, 244.
Schemnitz, 469, 493.
Schliessemaar, 158–9.
Scotland, 278, 498.
Shropshire, 497–8.
Sierra de Gador, 95, 422.
Sierra Nevada, 429.
Silesia. *See* Tarnowitz.
Smethwick, 509.
Snailbeach, 95, 507, 516.
Somersetshire, 497–8.
Spain, 216, 222, 246, 417, 418, 425, 428, 434, 495, 499.
Staffordshire, 498.
Stolberg, 139, 143, 314, 494–5.
Swaledale, 214.
Sweden, 296, 482, 499.
Tajova, 185.
Tarnowitz, 84, 139, 154, 157, 190, 204, 242, 357, 473, 482, 494.
United States, 278, 289.
Vialas, 346.
Villaricos, 429.
Villefort, 455.
Wales, 217, 229, 261, 418, 498.
Wanlock Head, 444.
Westmoreland, 497–8, 530.
Wisconsin, 278.
Yorkshire, 214, 497.
Zellerfeld, 369.
Lead-smoke, filtration of, 448.
Lead-speise, 376.
Lead-wire, 2, 7.
Leadhills, Plattnerite found at, 24.
——, immunity of miners from lead-poison at, 524.
Leathart, Mr., on Dr. Richardson's supposed invention of lead-softening process, 462.
Lehzen on lead from regulus, 493.
Levol on peroxide of lead, 26, 27.
—— on sulphide of lead and ferrocyanide of potassium, 63.
Lill, Von, his analysis of Abstrich, 201.
—— on composition of different kinds of lead, 439.
Lime and protoxide of lead, silicates of, 36.
——, alumina, and protoxide of lead, silicate of, 36.
—— and sulphate of lead, 42; with fluoride of calcium, 44.
——, sulphide of lead, and carbon, 55.
—— in Flintshire furnace, 236.
——, Schlieg-smelting with, in Rachette furnace, 392.
——, Carbonate of. *See* Carbonate of lime.
——, Plumbate of, how made, 25.
——, Sulphate of, with fluoride of calcium, and sulphates of lead and baryta, 44.
Linares, lead-smelting at, 247, 252.
"Linnets," 433, 434.

Liquation of cupriferous lead, 91; of hard lead, 467.
——— and poling at Schemnitz Silver Works, 469.
List of British lead-smelters, 497.
Litharge, odour of, 9.
———, crystals of, 12.
———, colours of, 12.
———, black, 201; "burnt," 13; "coarse," 13; "flake," 13.
———, action of water on, 16.
———, *fusibility of*, with metallic oxides, 17.
———, oxidizing action of, 18; with antimony, 19; arsenic, 19; bismuth, 20; copper, 21; iron, 21; selenium, 19; sulphur, 18; tellurium, 19; tin, 20; zinc, 21.
———, dezincification of lead by, 172.
——— in German cupellation, 195; metallic impurities in, 201; silver in, during process, 203, 204; in poor and rich cupellation, 207.
———, reduction of, in blast-furnace, 302, 476; in German cupellation-furnace, 479; in reverberatory furnace, 470, 473.
——— from pattinsonized lead, 476.
——— and china-clay, 489.
———, revived, lead from, 493.
———, lead revived from, by coke, 493; by charcoal, 493.
———, lead by revival of, from pattinsonized lead, 493.
———, sulphide of iron heated with, 533.
See Protoxide of lead.
Lithargification, German proverb on, 190.
Llanelly Lead-works, crane at, 127.
———, cupelling-furnaces at, 178.
London crucible for assaying lead-ore, 104.
Löwig on Tarnowitz lead, 368, 494.
Lustre of lead, 1.

M.

Machinery, application of, to Pattinson's process, 140.
Magnetic pyrites with galena, 95.
——— oxide of iron crystals in furnace-bed, 326.
Malleability of lead, 2.
"Manchia," 412.
Manganese, protoxide of, with protoxide of lead, 17.
———, black oxide of, and sulphide of lead, 54.
——— in galena, 95.
——— and lead, 93.
Manufacture of litharge, 12.
——— of peroxide of lead, 26.
——— of white-lead, 68, 508.
——— of oxychloride of lead, 78-84.
——— of blue vitriol, 333, 335.
——— of milled lead, 502.
——— of flint-glass, the best red-lead for, 507, 516.
——— of red-lead, 508; poisonous effects of, 520.

Marguéritte on sulphate of lead and chloride of sodium or potassium, 43.
Marignac, his atomic weight of lead, 10.
Marl for bed of cupellation-furnace, 185, 188.
Marseilles, lead-smelting at, 244.
Massicot, 12.
Mather and Co., their chambers for condensation of lead-smoke, 450.
Matlock, lead-smelting near, 241.
Matlockite, 79.
Matthiessen, Mr., on specific gravity of lead, 3.
——— on electric conductivity of lead, 8.
Maubach, Bischof's process at, 434.
Mechernich, Cordurie's process at, 171.
——— lead-smelting at, 352.
——— composition of lead from, 495.
Melting-point of lead, 8.
Melville, Mr., on lead perforated by insects, 522.
Mendip hills, present mining in, 497.
Mendipite, 79.
Merionethshire, production of lead-ore, lead, and silver in, 498.
Metallic phosphides, Pelletier on, 74.
Metals associated with galena, 95.
———, influence of, upon assay with fluxes in iron crucible, 117.
———, their effect upon Pattinson's process, 138.
——— eliminated from lead by crystallization, 144.
Michaelis on lead in dezincification, 163.
Milk an antidote to lead-colic, 529.
Milled sheet-lead, 501.
Miller, Prof., on concretionary deposit on red-lead oven, 520.
Mimetesite, 74, 100.
Mines, lead, infrequency of lead-poisoning in, 523.
Mining Company of Ireland, red-lead manufacture by, 514.
Minium, 24, 508, 528.
———, substitute for, in glass-making, 43.
Mispickel with galena, 95.
Missouri, lead-smelting in, 213.
Mitscherlich on crystals of litharge, 12.
——— on crystallized protoxide of lead, 13-15.
Molybdæna, 94.
Monocarbonate of lead, 70.
Mononitrate of lead, 85.
Mont Blanc, Dr. Tyndall's experiments on combustion at summit of, 277.
Montgomeryshire, production of lead-ore, lead, and silver in, 498.
Mrázek, Prof., on antimony, copper, and iron in cupellation, 202.
———, on roasted ore, 308.
———, on regulus in slags, 401.
———, on lead-smelting products, 405-410.
Muffle, refining in test with blast under, 112.
Mühlengasse works, lead-smelting at, 354.
Muldener Hütte, Freiberg, octahedral lead-crystals from, 2.

MÜLLER.

Müller on crystallized alloy from Ems and Holzappel, 378.
Munby, Mr., on Spanish plants used as fuel, 424.
Münsterbusch, lead-smelting at, 355.
Murchison, Sir R., on the geological age of the Harz mountains, 368.
——, Dr., on case of convulsions ascribed to lead-poisoning, 526.

N.

Nagybánya, composition of lead from, 493.
Nantes, lead-smelting at, 244.
"Naples Yellow," 87.
Narbrough, Sir J., on corrosion of iron-work of ships, 502.
Native amalgam at Sala, 296.
Nent Head, Stagg's condenser at, 441.
Neusohl, composition of lead from, 493.
Neutral carbonate of protoxide of lead, 70.
—— nitrate of lead, 85.
Nevill, Mr. C., his drawing of crane at Llanelly, 128.
——, Mr. W., on Parkes' process, 149-153.
——, Messrs., their cupelling-furnaces, 178.
Neville, Mr. J., his use of water-shower for lead-fume condensing, 446.
Newcastle-on-Tyne, litharge-reduction furnace at, 471.
Newton, Keates, and Co., their lead-smelting works, 239.
—— ——, use of Australian lead-ore by, 430.
—— ——, use of tea-lead for making gas-pipes by, 507.
New York, first ore-hearth in, 289.
Nicias, first use of red-lead for painting by, 509.
Nickel, its separation from lead by crystallization, 144.
—— and cobalt, concentration of, in speise, 318.
——, antimony, and copper alloy from smelting-furnace, 378.
Nickles on sulphate of lead and chloride of sodium or potassium, 44.
"Niederschlagsarbeit," 357, 405.
Nitrate of lead, action of zinc and cadmium on, 11.
—— ——, protoxide of lead from, 15.
—— of soda for softening hard lead, 465.
Nitrates of lead, 85; basic, of protoxide of lead, 85.
Nitre, &c. and sulphide of lead, 53.
Nitric acid, solubility of lead in, 10.
——, its action on sulphide of lead, 37; on sulphate of lead, 40.
Nitride of lead, 85.
Nitrites of protoxide of lead, 85.
Nitrogen and lead, 85.
Nolte on sulphide of lead and iron, 56-58.
—— on iron and galena, 375.

OXIDE.

North of England slag-hearth, 411.
Northumberland, lead-smelting in, 216.
——, lead-smelters in, 497.
—— production of lead-ore, lead, and silver in, 498.
"Nose" in blast-furnace, 371.

O.

Odour of lead, 9.
—— of litharge, 9.
——, aromatic, from Spanish smelting-works, 256.
"Ofenbruch," 377.
Ohme on lead-regulus from Clausthal, 373.
Oker, roasting of lead-regulus in kilns at, 393.
—— Smelting-works, copper-slag from, 388.
Old Testament allusion to refining of lead, 177.
Ophthalmia, use of "alquifoux" for, 94.
Opium, use of, for lead-colic, 526.
Opticians' glass, 35.
Orange-lead, 13, 70, 514, 516.
Orange-mine, 70.
Ore, white-lead, 70.
—— for Flintshire-furnace charge, 234.
—— and slag-smelting in reverberatory furnace, 323.
Ores and products, oxidized, smelting of, 411.
—— of lead. *See* Lead-ores.
Ore-hearth, introduction of, 216.
——, description of, 222, 278.
—— in Derbyshire, 278; at Keld Head works, 279, 282; Przibram, 481.
—— compared with reverberatory furnace, 284, 480.
——, variations in construction of, 285.
——, American, 289; at Bleiberg, 292; at Przibram, 293.
—— with Stagg's condenser, 457.
——, reduction of galena in, 481.
—— process, M. Gruner on, 491.
Ore-roasting at Freiberg, 307.
Ore-smelting at Freiberg, costs of, 332.
Osann on slag from slagged ore, 356.
Oven, drossing, concretionary matter from, 520.
Ovens for red-lead manufacture, 509.
Overbeck on peroxide of lead, 27.
Oxidation of lead and copper by atmospheric action, 92.
——, atmospheric, softening hard lead by, 459–464; special agents of oxidation, 464.
Oxide of antimony with protoxide of lead, 18.
——, carbonic, and sulphate of lead, 52; and sulphide of lead, 52.
—— of copper, sulphide of lead with, 534.
—— of iron, carbon, and sulphide of lead, 58.
—— ——, magnetic, crystals of, in furnace-bed, Freiberg, 326.

Oxide of iron, in smelting lead-ores, 359.
—— of lead, crystalline, reduction of, 15.
—— of manganese, black, and sulphide of lead, 54.
—— of silver and protoxide of lead, 16.
—— of zinc with protoxide of lead, 17.
Oxides, metallic, fused with protoxide of lead, 17.
Oxidized ores and products, smelting of, 411.
Oxidizing action of litharge, 18.
—— oven for red-lead making, 509.
Oxychloride of lead (Pattinson's), 38, 78, 79.
—— ——, manufacture of, 81.
—— ——, specific gravity of, 84.
Oxychlorides of lead, 79, 100.
Oxygen and lead, 10.
—— in grey-slag, 237.

P.

Painters' colic, 524.
Pallières, ores of, 346.
Par, smelting in flowing-furnace at, 257.
Parkes, Mr., his patent for separation of silver from other metals, 148.
——, his process, 148; cost of, 153; Karsten's experiments on, 153; the process in Prussia, 171.
Pary's mountain, anglesite at, 99.
Patent (Baker's), softening hard lead, 465.
—— (Cookson's), reduction of lead-ores by iron, 359.
—— (Cordurié's), dezincification of desilverized lead by steam, 167.
—— (Courage's), use of steam in lead-fume condensation, 446.
—— (Dick's), antimoniate-of-lead pigment, 87.
—— (Dobbs'), for adhesion of tin and lead, 9.
—— (Flach's), extraction of silver from lead, 162.
—— (Lord Grandison's), lead-smelting in reverberatory furnace, 218.
—— (Hall's), softening hard lead, 462.
—— (Herbst and Wassermann's), dezincification of lead by chloride of lead, 160.
—— (Hodges'), lead-smelting in reverberatory furnace, 218.
—— (Johnson's), dissolving oxide of lead from cupels, 464.
—— (Neville's), use of water-shower in lead-fume condensation, 446.
—— (Parkes'), separation of silver from other metals, 148.
—— (Pattinson's), separation of silver and lead, 121.
—— (Pontifex and Glassford's), softening hard lead, 464.
—— (Richardson's), use of steam in lead-fume condensation, 446.
—— ——, sugar-of-lead from dross in softening lead, 464.

Patent (Spence's), separating zinc from its ores, 405.
—— (Stagg's), lead-fume condensation, 441.
—— "Turner's Patent Yellow," 80.
—— (Warner's), softening hard lead, 465.
—— (Watson's), use of steam in lead-fume condensation, 444.
—— (Worsley's), separation of silver and lead, 140.
—— (Young's), use of steam in lead-fume condensation, 446.
Pattinson, Mr., his oxychloride of lead, 38, 78-84.
——, on sulphide of lead and steam, 50; with lime, 55.
——, crystals of lead from his process, 67.
——, his life and works, 121; his process for extraction of silver from lead, 121; description of process by himself, 129; modifications in, 134; cost, &c. of, 139; application of machinery to, 140; concentration of copper in, 146; effect of antimony upon, 147; effect of tin, 148.
——, on amount of lead converted into litharge on certain test, 184.
——, on the ore-hearth, 216, 285.
——, on North of England slag-hearth, 417.
——, on coal consumed in litharge-reduction, 472.
Pattinson desilverization pot, "lead-moss" on, 3.
Pattinsonization of softened lead, 461.
—— with liquation of hard lead, 468.
—— pot-dross from, 472.
Pattinsonized lead, analysis of, 493.
"Pava" (slag-hearth), 412.
"Pavo" (Carthagena furnace), 421.
Payen on crystalline protoxide of lead, 14; on hydrated protoxide of lead, 22.
Pearl-spar (dolomite) with galena, 95.
Peat-fuel used at Keld Head works, 281.
—— for smelting-furnace, 482.
Peligot on milk for lead-workmen, 529.
Pelletier on metallic phosphides, 74.
Pembrokeshire, production of lead-ore, lead, and silver in, 498.
Perforation of lead by insects, 521.
Peroxide of lead, 24; for softening hard lead, 465.
—— of manganese for softening hard lead, 465.
—— of tin, 17.
Person on specific heat of lead, 8; on melting-point, 8; on latent heat, 8.
Peru, lead-smelting in, 215, 271.
——, metallic riches in, 273.
——, silver and gold in galena of, 273.
——, Flintshire furnace in, 274.
——, lead-smelting at great elevations in, 274.
Petitgand, M., on lead-ores of Sierra de Gador, 95.
——, on Spanish reverberatory furnaces, 246.
——, on "boliches," 252-256.

PETITGAND.

Petitgand, M., on modified Bleiberg furnace, 270.
——, on "fourneau à manche," 412.
——, on Spanish slag-hearths, 417, 418.
——, on Carthagena furnaces, 421–429.
Phillips, Mr. E. M., on double furnace at Bleiberg, 268.
——, Mr. J. A., on white-lead, 70.
——, on treatment of galena by washing, 96.
——, on amount of lead from fume, 457.
——, on cast-iron bottom of softening-furnace, 459.
——, on cost of reduction of litharge, 473.
——, Prof., on Roman lead, 213, 214.
—— and Rivot on reduction of artificial sulphate of lead, 431.
Phosphate of lead, 99.
—— ——, assay of, 112.
—— ——, ores containing, 433.
—— of protoxide of lead, 75; with chloride of lead, 77.
Phosphide of lead, 74.
Phosphides, metallic, Pelletier on, 74.
Phosphorus and lead, 74.
Physical properties of lead, 1.
Pig-lead, Roman, 213, 214.
——, "W. B.," 508.
Pig-iron from copper-slags, 390.
Pigs of slag-lead, sound of, 517.
"Pilgrims' signs," fictitious, 67.
Pipe, Lead, 506; crust on, 535.
Pirath and Jung's works, Parkes' process at, 158.
—— ——, dezincification of lead at, 161.
—— ——, composition of lead from, 495.
Plagionite, 98.
Plants for fuel in Spanish smelting-works, 256, 425.
Plate-lead, 501.
Plattner on roasting galena, 46.
—— on roasting sulphides of lead and iron, 47.
—— on German cupellation, 197.
—— and Richter on refining of "Blicksilber," 211.
—— on American ore-hearth at Bleiberg, 292.
—— on lead-smelting at Freiberg, 303.
—— on blast-furnace regulus, 312; blast-furnace slags, 314.
—— on crystallized compounds in furnace-beds, 325, 326.
—— on sulphate of baryta in treatment of copper-regulus, 334.
—— on sulphides of zinc and iron in furnace incrustations, 377.
—— on smelting of regulus in the Harz, 380–382.
——, his specimens of accidentally produced red-lead, 519.
Plattnerite, 24.
Pliny, his designation of lead and tin, 1.
—— on galena, 94.
—— on lead in Britain, 214, 215.
—— on minium, 508, 509.

PROTOXIDE.

Pliny, on protection of workers in minium, 528.
Plumbate of baryta, how made, 25; of lime, 25; of potash, 25; of soda, 25.
Plumbers, their opinion of cast and milled lead, 502.
——, lead for pipes preferred by, 507.
Plumbic acid, 24.
"Plumbum candidum," 1.
"Plumbum corneum," 78.
"Plumbum nigrum," 1.
Point, smelting in flowing-furnace at, 257.
Poisoning by lead, 523; lead-colic, 526; lead-palsy, 527; preventive measures, 527; poisoning of animals, 530.
—— in red-lead manufacture, 520.
Poitou, lead-colic in, 524.
Poling of softened lead before pattinsonization, 461.
—— at Schemnitz Silver Works, 469.
Pontgibaud, German cupellation at, 203.
——, lead-smelting at, 338.
——, lead-fume from furnaces at, 452, 454.
Pontifex and Glassford, Messrs., their process for softening hard lead, 464.
—— and Wood, Messrs., composition of their refined lead, 494.
Potash, carbonate of, and sulphide of lead, 53.
——, caustic, and sulphide of lead, 53.
——, plumbate of, how made, 25.
—— and protoxide of lead, silicates of, 35.
Potassium and lead, 88; double sulphide of, 38.
——, chloride of, and sulphate of lead, 43.
——, cyanide of, and sulphate of lead, 45; and sulphide of lead, 63.
——, ferrocyanide of, and sulphide of lead, 63.
——, iodide of, its use for lead-palsy, 527.
Potters' ore, 94.
Pottery glazing, substitute for galena in, 43.
Pouchet, M., on lead perforated by insects, 522.
Poullaouen, lead-smelting at, 244.
——, smelting experiments at, 487.
Precipitation process, 219, 357.
Pressure, resistance of lead to, 4.
Production of silver and lead at Sala, 303.
—— of silver, lead, &c. at Freiberg, 337.
—— of lead in France, 338.
—— of lead-ore, lead, and silver in the United Kingdom, 498.
—— of lead in foreign countries, 499.
Products, oxidized, smelting of, 411.
Protosulphide of iron, silicate of lead with, 31.
Protoxide of copper with protoxide of lead, 17.
—— of iron, lead-smelting with basic silicate of, 384.
—— of lead, 12.
—— ——, crystallized, by wet methods, 13.
—— ——, reduction of, 15.

PROTOXIDE.

Protoxide of lead, a conductor of electricity, 15.
—— ——, its solubility in water, 15.
—— —— as an acid, 16; as a base, 16.
—— —— and oxide of silver, 16.
—— ——, fusibility of, with metallic oxides, 16; with acid (antimonious), 18; (arsenic), 18; (arsenious), 18; (stannic), 17; (titanic), 18; with antimony (oxide of), 18; with copper (dioxide of), 17; (protoxide of), 17; with iron-scales, 17; with iron (sesquioxide of), 17; with manganese (protoxide of), 17; with zinc (oxide of), 17.
—— ——, hydrated, 22.
—— —— and sulphate of lead, 43; sulphide of lead, 45.
—— ——, antimoniate of, 86.
—— ——, arseniates of, 73; with chloride of lead, 74; arsenites of, 73.
—— ——, carbonates of, 67; neutral carbonate, 70.
—— ——, nitrates of, 85; mononitrate, 85; basic nitrate, 85; hyponitrates and nitrites, 85.
—— ——, phosphates of, 75; with chloride of lead, 77.
—— ——, silicates of, 27. *See* Silicates.
—— ——, sulphate of, 40. *See* Sulphate of lead.
—— of manganese with protoxide of lead, 17.
Prussia, Parkes' process in, 171.
Przibram, American ore-hearth at, 293.
——, lead-smelting at, 398.
——, reduction of litharge at, 479.
——, ore-hearth at, 481.
——, composition of lead from, 493.
Puce-coloured oxide of lead, 24.
Pumpelly on iron-reduction process in Japan, 384.
Purchase of ores, 496.
Pure lead, 3.
Pyrites in magnetic ore at Fahlun, 326.
Pyrolusite used for the eyes, 94.
Pyromorphite, 77, 99.

Q.

Quartz with galena, 95.
Quicking glass, 1; lead crystals formed in process, 1.

R.

Rachette furnace, 385, 392.
" Raffiniren," 209.
Rammelsberg on Abstrich, 200.
—— on bournonite, 98.
—— on jamesonite, 98.
—— on lead-regulus, 373, 374; on regulus from smelting lead-regulus, 383.
—— on litharge-crystals, 12.

REGULUS.

Rammelsberg on pyromorphite with arsenic acid, 100; on fluor-apatite in pyromorphite, 100.
—— on sulphide of lead, 37.
Rammelsberg copper ores, 388.
Rasp for working lead, 2.
Ratcliffe, Mr., on lead-smelting in Peru, 271.
——, on smelting at high elevations, 275, 276.
Rawson, Barker, and Co.'s columnar lead, 2.
—— white-lead from decopperized Derbyshire slag-lead, 176.
—— Spanish slag-hearth, 419.
—— manufacture of red-lead, 512.
Reactions, special, with sulphide of lead, 45.
Real Compania Asturiana, composition of their lead, 495.
Red-argol in assay of lead-ore, 106.
Reden, Von, on seven-twyer furnace in the Harz, 316.
Red-lead, 24; its change of colour when heated, 13; changed from white-lead, 70.
—— for glass-making, lead suitable for, 507, 516.
—— known to the ancients, 508.
——, manufacture of, 508.
—— ovens, 509.
——, poisonous effect of, 516, 520.
——, accidental production of, 519.
——, concretionary matter in making, 519.
Reducing agents for assay of lead-ore, 106.
Reduction of litharge, 470; in Bleiberg furnace, 473; in German cupellation-furnace, 479; Chinese method, 479.
—— of silicate of lead by iron, 533.
Rees, Dr. Owen, on lead-colic, 525–527; on lead-palsy, 527.
Refining or cupellation, 177.
—— in open test with blast, 209.
—— " Blicksilber," 209.
——, Indian method of, 211.
—— in a test with blast under a muffle, 212.
Regnault on specific heat of lead, 8.
—— on sulphide of lead heated in vapour of water, 49, 50.
Regulus from lead-smelting operations, at Clausthal, 373; Freiberg, 306–337; Lautenthal, 373; Pontgibaud, 343; Przibram, 406, 411; Upper Harz, 372, 382, 383.
——, Lead, regulus from, 383; slags from, 383; lead from, 493.
——, sulphate of lead in, 380; silver in, 381.
—— from Schlieg-smelting with cast-iron, 391.
—— from Rachette furnace and Schlieg-ofen, 393.
——, diffusion of, in slags, 401; retention of, 410.
——, formation of, by iron-pyrites, in Flintshire furnace, 483.
—— from smelting Australian lead-ore, 538.

REICH.

Reich on specific gravity of pure lead, 3.
—— on increase of specific gravity of lead by rolling, 4.
—— on liquation of cupriferous lead, 91.
—— on Pattinson's process, 137, 138.
—— on regulus in Freiberg process, 317; enriched regulus, 334.
—— on manufacture of blue vitriol from copper-regulus, 333.
Resistance of lead to pressure, 4.
Reverberatory furnace, 216, 222; Bleiberg furnace, 222, 261; Carinthian, 269; Flintshire, 218 (*see* Flintshire furnace); Flowing, 218, 222, 257, 261; Spanish, 222, 246.
——, smelting in, at high elevation, 274.
—— compared with blast-furnace, 491; with ore-hearth, 284, 480.
——, slag- and ore-smelting in, 306, 319, 332.
——, accessory products from bed of, 325.
——, treatment of copper-regulus in, 333.
——, reduction of artificial sulphate of lead in, 431.
—— for softening hard lead, 460.
——, reduction of litharge in, 470.
—— with peat fuel, 482.
Rhodes, Mr., on casting sheet-lead, 500.
Richardson, Dr., his manufacture of lead pigment, 81.
—— on softening hard lead, 461; by atmospheric oxidation, 462; softening lead from dross, 466.
—— on Chinese tea-lead, 464.
—— on sugar-of-lead from dross in softening lead, 464.
—— on cost of reduction of litharge, 473.
——, his use of steam for lead-fume condensing, 446.
Richter, Prof., on refining of "Blicksilber," 211.
—— on lead-smelting at Freiberg, 303.
—— on calcining, 307.
—— on blast-furnace lead, 312; blast-furnace slags, 314.
—— on Stolberg and seven-twyer furnaces, 314.
—— on regulus from slag, 318; on copper regulus, 334.
—— on litharge-slags, 476; on reverberatory furnace slag, 324; on slags from slag- and ore-smelting with carbon, 325.
Ripon, lead-mines at, 214.
Rivot on galena and lime, 55.
—— on lead-smelting at Bleiberg, 264, 269, 270; in France, 338; in the Harz, 369; Poullaouen, 245; Tarnowitz, 364; Vialas, 346.
—— on slag from lead-smelting, 349.
—— on raw pit-coal fuel, 364.
—— on reduction of artificial sulphate of lead, 431–433.
—— on lead-fume, 452.
—— on blende in blast-furnace, 484.

SCHEURER.

Rivot and Zeppenfeld on silver in litharge during cupellation, 203.
Roasting and deoxidizing process, 296.
—— and reaction method, 491.
Rodwell, Mr., on absorption of oxygen by sulphide of lead, 47.
—— on sulphide of lead and carbonic oxide, 52.
—— on sulphate of lead and hydrogen, 52; and carbonic oxide, 52.
Rœssler, H., on German lead, 495.
"Rohstein," 306.
Rolled sheet-lead, 501.
Rolling, casting of lead for, 503.
Roman lead, atmospheric incrustation on, 67.
—— ——, production of, in Britain, 213.
—— —— slags, Spanish slag-hearth for, 418.
—— ——, workers of, precaution taken by, 528.
—— ore and slag, where now smelted, 497.
Rose, G., on lead-regulus crystals, 372.
Rossie (New York), ore-hearth at, 289.
Rothehütte, treatment of copper-slags at, 389, 390.
Rothschilds, Messrs., Cordurié's process at their Havre works, 169.
Rouen, machinery applied to Pattinson's process at, 143.
Royal Arsenal, bullets made from rods of lead in, 3.
Royal School of Mines, description of Pattinson's process prepared for, 129.
—— —— Laboratory, iron crucible used in, 104, 108.
—— —— Museum, action of air on crystals of lead in, 67; Pattinson's ladle in, 127; model of lead-fume condenser in, 444.
Rudberg on melting-point of lead, 8.
—— on alloys, 468.
Rugby, cows poisoned by "bullet-spray" at, 532.

S.

Sala, lead-smelting at, 296; blast-furnace at, 298.
Salt used in dezincification of lead at Clausthal, 161.
Sampling of lead-ore, 103.
Sandmann on manganese in galena, 95.
Sandstone, galena in, 352.
Sardinia, production of lead in, 499.
Savoy, lead-smelting in, 244.
Schaffner on hydrated protoxide of lead, 22.
Scheele on oxychloride of lead, 80.
Scheerer on crystallized compounds in furnace-beds, Freiberg, 325, 326.
Schemnitz, composition of lead from, 493.
—— Silver Works, liquation and poling at, 469.
Scheurer-Kestner on erosion by insects of lead of sulphuric acid chamber, 521.

"Schliech"-smelting at Tarnowitz, 360–367.
"Schliegöfen," 392, 393.
"Schlieg"-smelting, 369-383.
——, cast-iron from lead-slags used in, 391.
—— with lime in Rachette furnace, 392; with copper-ore slags, 392.
Schliessemaar, desilverization of lead by zinc at, 158, 159.
Schlüter on reverberatory furnace, 216.
Schnederman on sulphate of lead with carbonate of lime, fluoride of calcium, and carbon, 44.
Schulzite, 98.
Scotland, ore-hearth in, 278.
——, list of lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
Selenide of lead, 100.
Selenium and litharge, 19.
Serullas on lead and potassium, 89.
Sesquioxide of iron with protoxide of lead, 17; with sulphide of lead, 56; with silicates of protoxide of lead and charcoal, 34.
—— of lead, 23.
Seven-twyer furnace, 314-316.
Sewell, Mr., white-lead made by, 69, 334.
Sewen, M., on lead-smelting at Sala, 296.
Sheep's dung used for fuel, 276.
Sheet-lead, cast, 500; rolled or milled, 501.
Ships sheathed with milled lead, 502.
Shot, alloy for making, 71; arsenic in, 72.
Shropshire, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Sibson, Dr., on iodide of potassium for lead-colic, 527.
"Siebenförmiger Ofen," 314.
Siebold on insolubility of protoxide of lead in water, 16.
Sieger on Flach's system, 164.
Sierra de Gador, ores of, 95, 422.
Sierra Nevada, Carthagena furnace in the, 429.
Silesia, Parkes' process in, 171.
——, composition of lead from, 494.
See Tarnowitz.
Silica and sulphate of lead, 42.
——, its influence in assay of galena, 114.
——, free, effect of, in smelting galena, 346.
—— in lead-ore, its effect on smelting, 487.
Silicate of lead and sulphide of lead, 48.
—— ——, reduction of, by iron, 533.
—— of protoxide of iron (basic), lead-smelting with, 384; (tribasic), with sulphide of lead, 58.
—— of protoxide of lead, 27; colour of, 28, 29.
—— of protoxide of lead with baryta, 36;

with charcoal, 31; iron, 33; iron (protosulphide of), 31; iron (sesquioxide of) and charcoal, 34; lime, 36; lime and alumina, 36; lime (carbonate of) and charcoal, 33; potash, 35; soda, 36; soda (carbonate of) and charcoal, 33; sulphur, 30.
Silicates, certain, and sulphate of lead, 42; in lead-ore, their effect on smelting, 489.
Silicon and lead, 27.
Silver, importance of litharge in metallurgy of, 18.
—— in blende, 399; in British lead-ores, 102; in galena, 95-97, 399; in litharge, 201; in ores of lead, 219; in Przibram galena, 398.
——, its influence upon assay with fluxes in iron crucible, 117.
——, extraction of, from lead, 121; Pattinson's process, 121; Parkes' process, 148; Cupellation, 177.
——, effect of, on melting-point of lead, 137.
——, its effect in Pattinson's process, 138.
——, extraction of, from zinc, 163.
—— in lead and litharge during cupellation, 203, 204.
——, occurrence of, at Sala, 296.
—— and lead at Sala, production of, 303.
—— in roasted lead-regulus, 381.
—— from Schlieg-smelting in Rachette furnace, 393, 397.
—— from mines of Carthagena, 422.
—— in lead-fume, 455.
——, production of, in the United Kingdom, 498.
——, table for computing from percentage of, the troy weight of silver per statute ton, 538.
——, Oxide of, and protoxide of lead, 16.
——, Sulphide of, in lead-ore, its effect on smelting, 486.
——, White capillary, in furnace-bottom, 326.
Silver-lead from Upper Harz Works treated by Cordurié's process, 536.
Silver-mines of Carthagena, 422; of Laurium, 418.
Sims, Willyams, Nevill, and Co.'s works, Parkes' process at, 149.
"Sinterröstöfen," 307.
Sirex gigas, lead eroded by, 521.
Slag- and ore-smelting in reverberatory furnace, 323; slags from, 324; cost of smelting, 332.
Slags for furnace-bed, 228.
—— from Lea Smelting Works, 241.
—— in Bleiberg furnace, 265.
—— from ore-hearth at Keld Head, 282.
—— from American ore-hearth at Bleiberg, 292; at Przibram, 293.
——, blast-furnace, 313.
——, seven-twyer furnace, 315, 316.
—— from smelting of regulus, 317, 318.
—— from smelting Friedrichsgrube galena, 366.

SLAGS.

Slags from smelting "Schlieg," 378; in Rachette furnace, 393, 394.
—— from lead-regulus smelting, 383.
——, diffusion of regulus in, 401; retention of regulus in, 410.
—— from Spanish slag-hearth, 417, 420.
—— from reduction of dross, 475; of litharge, 476; of silicate of lead by iron, 533.
——, Copper, for reduction of galena, 385, 387.
—— ——, reducibility of iron in, 388.
—— ——, cast-iron from, 388; pig-iron from, 390.
——, Copper-ore, Schlieg-smelting with, 392.
——, Grey, for furnace-bed, 229.
—— ——, from Flintshire furnace, 235, 242.
—— ——, from Spanish reverberatory furnace, 251.
—— ——, in flowing furnace, 261.
—— ——, analysis of, by Ferientsik, 268.
—— ——, extraction of lead from, 412.
—— ——, in Carthagena furnace, 429.
——, Iron-finery, use of, in lead-smelting, 360, 368, 384.
——, Lead, and copper-slags, assays of, 389.
—— ——, reducibility of iron in, 390.
—— ——, cast-iron from, 391; slags with the cast-iron, 391.
—— ——, old, smelting of, 418.
—— —— (Roman), Spanish slag-hearth for, 418.
Slag-hearths, 411; at Keld Head, 412; in Spain, 417, 418.
——, Spanish, "linnets" smelted in, 434.
—— with Stagg's condenser, 457.
Slag-lead of Andreasberg, 174.
——, Derbyshire, decopperized, 176.
—— used in Baker's softening process, 465.
——, action of, in drossing, 517; antimony in, 517.
Slagged-ore, treatment of, 356.
Slimes ("Schliech") in lead-smelting, 360-367.
Smelting of lead-ores of Commern, 350.
—— of ores containing carbonate and phosphate of lead, 433; containing sulphate of lead, 430.
—— of roasted lead-regulus, 382.
—— of oxidized ores and products, 411.
Smelting processes, 220, 296, 357. *See* Lead-smelting.
Smethwick, red-lead ovens at, 509.
Smith, Mr. R., on protoxide of lead and arsenious acid, 18.
—— on litharge and antimony, 19; and iron, 21; tin, 20; zinc, 21.
—— on silicates of protoxide of lead heated with iron, 34.
—— on subsulphide of lead, 39.
—— on sulphate of protoxide of lead, 41, 42.

SPAIN.

Smith, Mr. R., on sulphate of lead with fluoride of calcium, 44; with lead, 45.
—— on sulphates of lead, baryta, and lime, and fluoride of calcium, 44.
—— on sulphide of lead with ferrocyanide of potassium, 64; with tin, 60; zinc, 61.
—— on arsenic in shot, 72.
—— on antimoniate of protoxide of lead, 86.
—— on lead and potassium, 89.
—— on silver and gold in galena, 97; in lead, 96; in lead-fume, 455.
—— on Australian lead-ore, 430; on regulus from, 538.
—— on Alport "linnets," 433.
—— on concretionary deposit on red-lead oven, 520.
Smoke from lead-smelting furnaces, 436; filtration of, 448.
Smyth, Mr. Warington, on British lead-ores, 100.
Snailbeach mine, galena with arseniate of cobalt from, 95.
—— lead, red-lead prepared from, 507, 516.
Soap, charred, for alloy of lead and sodium, 90.
Soda and protoxide of lead, silicates of, 36.
——, Carbonate of, with charcoal and silicate of protoxide of lead, 33; with sulphide of lead, 53.
—— —— in assay of lead-ore, 106.
——, Caustic, and sulphide of lead, 53.
——, Hyposulphite of, its action on sulphate of lead, 42.
——, Plumbate of, how made, 25.
Soda-ash, reduction of lead from dross with, 466.
Soda-making, formation of sulphate of soda from sulphate of lead for, 44.
——, hydrochloric acid from, applied to white-lead manufacture, 81.
Sodium and lead, 90; double sulphide of, 38.
——, Chloride of, with sulphate of lead, 43; with sulphide of lead, 65.
—— ——, dezincification of lead by, 161.
Softening of hard lead, 458.
Solubility of protoxide of lead in water, 15.
Somersetshire, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Sophienhütte (Harz), lead-slags from, 390.
Sopwith, Mr., on flues for lead-fume condensing, 438.
Sorby, Mr., his microscopic investigations on iron and steel. 411.
Sound of lead, 2; of pigs of slag-lead, 517.
Spain, lead-smelting in, 216, 246.
——, slag-hearths in, 417.
——, plants used as fuel in, 425.
——, coal-fields in, 428.
——, production of lead in, 499.

SPANISH.

Spanish furnace (boliche), 222, 246.
—— lead, composition of, 495.
—— slag-hearth, 418; "linnets" smelted in, 434.
Specific gravity of lead, 3; increased by rolling into sheet, 4.
—— of galena, 37; of galena with manganese, 95.
—— of litharge crystals, 12.
—— of hard lead, 478; of oxychloride of lead, 84; peroxide of lead, 24; red-lead, 24; white-lead, 84; of lead of different kinds, 493.
—— of solution of copper-regulus in sulphuric acid, 336.
—— of lead-regulus, 373.
—— of optical glass, 35.
—— of slags from blast-furnace, 314; of slags from slag- and ore-smelting, 324; of slag and regulus, 410.
Specific heat of lead, 8.
Speise in Freiberg process, 313.
——, concentration of cobalt and nickel in, 318.
——, Lead, at Andreasberg, 376.
Spence, Mr., his treatment of galena and blende, 405.
Staffordshire, production of lead-ore, lead, and silver in, 498.
Stagg, Mr., his lead-fume condenser, 441, 457.
Stannic acid with protoxide of lead, 17.
Stas, his atomic weight of lead, 10.
Stassfurth salt for dezincification of lead, 162.
Steam, action of, on galena, 50.
——, dezincification of desilverized lead by, 167.
——, its application to lead-fume condensing, 436, 444, 450.
—— and zinc desilverizing process at Lautenthal, 535.
Stokoe's lead-fume condenser, 442.
Stolba on lead and boiling water, 10.
Stolberg, cost of Pattinson's process at, 139.
——, machinery applied to Pattinson's process at, 143.
—— furnace, 314.
——, composition of lead from, 494, 495.
Strabo on mines of Carthagena, 422.
Strahlstein with galena, 95.
Strauch, E., on Rachette furnace for Schlieg-smelting, 395.
Streng on specific gravity of lead, 3.
—— on Bleiberg lead, 267.
—— on copper-slags, 387, 390; lead-slags, 390.
—— on hard lead, 478.
—— on lead from revived litharge, 493.
—— on pattinsonized lead, 493.
Strickle used in making cast-lead, 500.
Strontianite with galena, 95.
Strychnine, use of, for lead-palsy, 527.
Sturm and Mrázek on antimony, copper, and iron in cupellation, 202.

SULPHIDE.

Sub-oxide of lead, 11.
Sub-sulphides (supposed) of lead, 39.
Sugar-of-lead from dross in softening hard lead, 464.
Sulphate of baryta, with sulphates of lead and lime, and fluoride of calcium, 44.
—— —— with galena, 95.
—— ——, its influence in assay of galena, 116.
—— ——, in treatment of copper-regulus, 334.
—— —— and coke-dust, carbonic acid from, 334; white-lead from, 334.
—— —— in lead-ore, its effect on smelting, 488.
—— of copper, made from copper-regulus, 333.
—— —— from argentiferous disulphide, 337.
—— ——, removal of sulphate of iron from, 337.
—— of iron in sulphate of copper, 337.
—— of lead, 40; with fixed alkaline carbonates or lime, 42; with silica and some silicates, 42; borax, 43; protoxide of lead, 43; chloride of lead, 43; alkaline and earthy sulphates, 43; chloride of sodium or potassium, 43; fluoride of calcium, 44; fluoride of calcium and lime, 44; carbonate of lime, fluoride of calcium, and carbon, 44; sulphates of baryta and lime and fluoride of calcium, 44; lead, 45; cyanide of potassium, 45; iron, 45; sulphide of lead, 46; carbon, 51; in hydrogen, 52; in carbonic oxide, 52.
—— ——, 98; action of hyposulphite of soda on, 42.
—— ——, assay of, 112.
—— —— in roasted lead-regulus, 380.
—— ——, smelting of ore containing, 430.
—— ——, artificial, reduction of, 431.
—— —— in fume, 458.
—— of lime with sulphates of lead and baryta and fluoride of calcium, 44.
Sulphates, alkaline and earthy, with sulphate of lead, 43.
Sulphato-carbonate of lead, 100.
Sulphide of antimony, with sulphide of lead, 38; with lead, 62.
—— —— in lead-ore, its effect on smelting, 485.
—— of arsenic and lead, 63.
—— of iron with litharge, 533.
—— of lead, 37, 94.
—— ——, with sulphide of antimony, 38; with other metallic sulphides, 38; protoxide of lead, 45; sulphate of lead, 46; access of air, 46; access of air in admixture with other sulphides, 47; silicate of lead, 48; in vapour of water, 49; in hydrogen, 52; in carbonic oxide, 52; with carbonate of soda or potash, or caustic soda or potash, 53; fixed alkalies or their carbonates and nitre, and nitre or other oxidizing substances, 53; fixed alkalies,

or their carbonates, and carbon, 54; lime, and lime and carbon, 55; baryta, and baryta and carbon, 55; sesquioxide of iron, 56; iron, 56; oxide of iron and carbon, 58; tribasic silicate of protoxide of iron, 58; tin, 59, 535; copper, 60; oxide of copper, 534; zinc, 61; antimony, 62; cyanide of potassium, 63; ferrocyanide of potassium, 63; chloride of sodium, and roasted with access of air, 65; chloride of ammonium, 66.
Sulphide of lead, special reactions connected with, 45.
—— ——, crystals of, produced in furnaces, 326, 376.
—— of silver in lead-ore, its effect on smelting, 486.
—— of zinc in lead-smelting furnaces, 377, 378.
—— —— in lead-ore, its effect on smelting, 484.
Sulphides of lead and antimony, 98.
——, double, of lead and sodium or potassium, 38.
——, metallic, heated with sulphide of lead, 38.
—— (Sub-) of lead, 39.
See also Galena.
Sulphur and litharge, 18.
——, silicates of protoxide of lead heated with, 30.
—— and lead, 37.
——, lead containing, for making red-lead, 518.
Sulphur-baths for lead-poisoning, 527.
Sulphuric acid and lead, 10.
——, solution of copper-regulus in, 335.
—— in lead-fume, 451, 452.
—— chambers, lead for, 507; lead of, eroded by insects, 521.
Swaledale, lead-smelting in, 214.
Sweden, lead-smelting in, 296.
——, use of peat for smelting-furnaces in, 482.
——, production of lead in, 499.

T.

Tables:—Tenacity of lead, 8.
—— Silicates of protoxide of lead, 29; with sesquioxide of iron and charcoal, 34.
—— Composition of optical glass, 35.
—— Sulphide and silicate of lead, 48.
—— Reduction of sulphide of lead by iron, 57.
—— Proportion of silver in galena and presence of gold, 97.
—— Silver in British lead-ores, 103.
—— Assay of galena with carbonate of lime, 113, 114; with silica, 114–116; with sulphate of baryta, 116, 117; with antimony, 119.
—— Lead treated by Pattinson's process, 133.

Tables:—Concentration of silver in Pattinson's process, 137.
—— Percentage of nickel in lead, 145.
—— Dezincification of lead, 162; by chloride of lead, 161.
—— Desilverization by zinc at Clausthal, 167.
—— Elimination of metals in desilverization by zinc, 176.
—— Antimony, copper, and iron in lead during cupellation, 202.
—— Silver in lead and litharges during cupellation, 204.
—— Cupellation at Friedrichshütte in 1864–5, 208.
—— Composition of charge for, and grey-slag from, Flintshire furnace, 235.
—— Composition of products of smelting galena at Bagillt, 239.
—— Smelting in Flintshire furnace at Tarnowitz, 243.
—— Results of Belgian compared with Flintshire furnace, 246.
—— Results of one week's smelting of same ore at Keld Head, 283.
—— Results from American ore-hearth at Bleiberg, 292.
—— Yields and loss in smelting lead-slags at Freiberg, 331.
—— Smelting-costs at Freiberg, 332, 333.
—— Lead-regulus from Upper Harz, 373.
—— Yield from Schlieg-smelting in Rachette furnace at Lautenthal, 396.
—— Assays of copper and lead-slags, 389.
—— Regulus and slag in Przibram smelting, 409.
—— Results from slag-hearth at Keld Head, 416.
—— Cost of reduction of grey-slags in Carthagena furnace, 429.
—— Loss of lead in blast-furnace smelting, 457.
—— Litharge-reduction at Tarnowitz, 475.
—— Composition of different kinds of lead analysed at Vienna, 493; at Clausthal, 494.
—— Lead-ore, lead, and silver production, 498, 499.
—— Imports and exports of lead, 499.
—— Result from zinc and steam desilverizing process at Lautenthal, 536.
—— Computing from percentage of silver the troy weight of silver per statute ton, 538.
Tajova, marl first used for cupellation at, 185.
Tarnowitz, native chlorocarbonate of lead at, 84.
——, cost of Pattinson's process at, 139.
——, desilverization of lead by zinc at, 154; cost, 157.
——, cupellation furnace-bed at, 190.
——, German cupellation with coal at, 204.
——, lead-smelting at, 242, 357; use of Flintshire furnace at, 242.

TARNOWITZ.

Tarnowitz, iron-reduction process at, 357.
——, Bleiberg furnace for reduction of pot-dross at, 473.
——, introduction of reverberatory furnace at, 482.
——, composition of lead from, 494.
Taste, absence of, in lead, 9.
Taylor, Mr. J., on cost of Pattinson's process, 139.
——, Messrs., their smelting-works at Pontgibaud, 338.
Tea-lead, 463, 464.
—— prepared by casting, 501.
——, use of, in making gas-pipes, 507.
Teichmann, M., on litharge in German cupellation, 195.
—— on German cupellation with coal, 204.
—— on lead-smelting at Friedrichshütte, 357.
Tellurium and litharge, 19.
"Temper" for lead-shot, 71.
Tenacity of lead, 7.
Test for cupellation, 180.
——, open, with blast, 209.
Thames, the, fictitious "Pilgrims' signs" from, 67.
Thénard, his white-lead, 69.
Thomas, Mr. E., on Indian coins, 212.
——, Mr. J. L., on lead-smelting at Linares, &c., 247, 255.
—— on cost of smelting in Carthagena furnace, 427.
Thornton, Mr., his drawings of lead-fume condenser, 447.
"Ticketings," 496.
"Times" on Laurium silver-mines, 418.
—— on lead-poisoning of cows, 531.
Tin, Pliny's designation of, 1.
—— and lead, 9; and litharge, 20; sulphide of lead, 59, 535.
—— and lead, crystallization of, 146.
——, its effect upon Pattinson's process, 148.
——, colours on melted lead affected by, 463, 464.
——, peroxide of, and litharge, 17.
Titanic acid with protoxide of lead, 18.
Todd, Dr., his sulphur-baths for lead-poisoning, 527.
Tookey, Mr., on specific gravity of pure lead, 3.
—— on lead and sodium, 90.
—— on ore for Flintshire furnace, 234; on grey-slag from, 235.
—— on Chinese litharge-reduction, 479.
—— on Snailbeach lead, 517.
"Touch-paper," 85.
Treble furnaces at Bleiberg, 268.
Tribasic silicate of protoxide of iron and sulphide of lead, 58.
Trowell Moor, sandstone with galena at, 352.
Tungsten and copper, 93.
Tunner, Von, on lead-smelting at Bleiberg, 261.
"Turner's Patent Yellow," 80.

WARD.

Tuson, Prof., on lead-poisoning of cows, 531.
Tutschnack, marl first used by, for cupellation, 185.
Tyndall, Dr., his experiments on combustion on Mont Blanc, 277.
Type-metal perforated by insects, 521.
——, its effect on compositors, 525.

U.

Ulrich on bismuthic litharge, 202.
United Kingdom, production of lead-ore, lead, and silver in, 498.
——, lead imports and exports, 499.
United States, lead-region of, 278.
——, ore-hearth in, 278.

V.

Vaillant, Marshal, his exhibition of eroded bullets, 521.
Vanadinite, 100.
Vauquelin on oxychloride of lead, 80.
—— on lead and potassium, 89.
Vesuvius, crystallized chloride of lead at, 77.
Vialas, lead-smelting at, 346.
Vienna, analyses of lead made at, 493.
"Villacher Blei," 267.
Villaricos, Carthagena furnace at, 429.
Villefort, fume from cupellation-furnace at, 455.
Volatilization of lead, 9; of protoxide of lead, 15.
—— of zinc in slag- and ore-smelting, 325.

W.

Waddell, Mr., his method of casting thin plates of zinc, 501.
Wages at Bleiberg, 267.
Wales, "cupolas" introduced from, 217.
——, lead-smelting in, 229.
——, flowing-furnace in, 261.
——, Spanish slag-hearth in, 418.
——, list of lead-smelters in, 498.
——, production of lead-ore, lead, and silver in, 498.
Walker, Mr. A., on fraudulent use of lead-smelters' names at Freiberg, 303.
Wanlock Head, lead-fume condensation at, 444.
Ward, Mr., on brown crust from oxidization of lead and copper, 93.
—— on slag from ore-hearth at Keld Head, 282.
—— on Australian lead-ore, 430.
—— on alloy from liquation of hard lead, 467.
—— on upper layer from sulphide of lead heated with tin, 535.
—— on crust formed on lead-pipe, 535.

WARNER.

Warner, his process for softening hard lead, 465.
Washing, its effect on galena, 96.
Washington Chemical Co., manufacture of oxychloride of lead by, 82.
Water, solubility of protoxide of lead in, 15; solubility of sulphate of lead in, 40.
——, sulphide of lead heated in vapour of, 49.
——, boiled, its action on monocarbonate of lead, 70.
——, boiling, its action on lead, 10.
——, cold, action of, on molten galena, 37.
——, distilled, action of, on lead, 68.
—— from lead-works, carbonate of lead in, 530.
Water-shower for lead-fume condensation, 446, 450.
Watson, Bishop, on smelting of lead-ore in Derbyshire, 214, 215.
—— on reverberatory furnace, 216, 218.
—— on ore-hearths, 278.
—— on smelting old lead-slags, 418.
—— on collection of lead-fume, 434.
—— on use of steam for lead-fume condensing, 446.
—— on colours on the surface of melted lead, 463.
—— on Chinese tea-lead, 507.
—— on concretionary matter in making red-lead, 519.
—— Mr. H., his method of condensing lead-fume, 446.
—— Sir T., on lead-colic, 525.
—— on lead-poisoning, 526; on lead-poisoning of animals, 530.
Way, Mr. A., on Roman lead, 213.
"W. B." pig-lead, 508.
Wedding, Dr., on lead-smelting at Friedrichshütte, 357.
—— on wet process for extracting lead from carbonated ores, 434.
—— and Bräuning on Parkes' process in Prussia, 171; on Cordurié's process at Lautenthal, 535.
"Weissbleierz," 99.
Welding of iron compared with cohesion of lead, 9.
Wertheim on tenacity of lead, 8.
Westmoreland, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
——, lead-poisoning of animals in, 530.
Weston, Mr., on ore for Flintshire furnace, 235.
—— on products of smelting galena in Flintshire furnace, 239.
—— on smelting process at Keld Head, 279.
—— on reverberatory furnace compared with ore-hearth, 284.
—— on slag-hearth, 412.
—— on slag from Spanish slag-hearth, 420.
—— on lead-fume condensing, 442.

YORKE.

Weston, Mr., on composition of lead-fume, 451.
Wet methods, crystallized protoxide of lead by, 13.
—— assay, inapplicability of, to lead-ores, 103, 120.
—— process for extracting lead from carbonated ores, 434.
White-argol in assay of lead-ore, 106.
White-lead, 68.
——, use of hydrochloric acid in making, 81.
——, specific gravity of, 84.
—— from decopperized Derbyshire slag-lead, 176.
——, sulphate of baryta and coke-dust applied in making, 334.
——, lead suitable for, 508.
——, injurious to workers in, 528.
—— ore, 70, 99.
——, use of "whiting" in making, 82.
Wiedemann and Franz on conductivity of lead for heat and electricity, 8.
Williams, Mr., on immunity of miners from lead-poison, 524.
—— on use of opium for lead-colic, 526.
Wilson, Dr. Geo., on lead-poisoning of animals, 530.
Winkelblech on reduction of crystalline oxide of lead, 15.
—— on hydrated protoxide of lead, 22.
—— on sesquioxide of lead, 23.
Winkler on German cupellation, 185–197.
—— on refining of "Blicksilber, 209.
—— on lead-smelting at Freiberg, 303.
Wire, Lead, 2, 7.
Wisconsin, reverberatory furnaces in, 278.
Wöhler on oxide of silver and protoxide of lead, 16.
—— on peroxide of lead, 27.
Workmen, their disregard of sanitary precautions, 529.
Worsley, Mr. P. J., on separation of silver and lead, 140.
Wright, the inventor of the Flintshire reverberatory furnace, 216, 218.
——, Mr. T., on Roman lead, 213.

Y.

Yield of silver in British lead-ore, 102.
—— of lead by assay affected by other metals and by non-metalliferous matters, 113–117.
—— from reverberatory furnace compared with ore-hearth, 284.
—— from Schlieg-smelting in Rachette furnace, 396.
Yorke, Col., his crystals of protoxide of lead, 14.
—— on solubility of protoxide of lead in water, 15.
—— on action of distilled water with air on lead, 68.

YORKE.

Yorke, Col., on monocarbonate of lead, 70.
Yorkshire, lead-smelting in, 214.
——, lead-smelters in, 497.
——, production of lead-ore, lead, and silver in, 498.
Young, Messrs., their use of steam for lead-fume condensing, 446.

Z.

Zellerfeld and Clausthal lead-ores, 369.
Zeppenfeld on silver in litharge during cupellation, 203.
—— on lead-smelting at Pontgibaud, 339.
Zinc, action of, on nitrate of lead, 11.
—— and litharge, 21; and sulphide of lead, 61.
—— in galena, 95; in litharge, 201.
——, its influence upon assay with fluxes in iron crucible, 118.
—— and lead, separation of, 148. *See also* Cordurié. Dezincification. Parkes.

ZOOLOGICAL.

Zinc, desilverization of lead by, 148, 154, 165; by zinc and steam, 535.
——, extraction of silver from, 163.
——, decopperization of lead by, 174.
—— in Flintshire furnace, 239.
——, volatilization of, in slag- and ore-smelting, 325.
——, Grimm's process for treatment of zinc and lead-ores, 404; Spence's process, 405.
——, colours on melted lead affected by, 464.
——, casting thin plates of, for galvanic purposes, 501.
——, Oxide of, with protoxide of lead, 17.
——, Sulphide of, in lead-smelting furnaces, 377, 378; in lead-ore, its effect on smelting, 484.
Zinckenite, 98.
Ziurek on Tarnowitz lead, 368, 494.
Zoological Gardens, encrusted lead-pipe from, 535.

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